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On the Contact Potential.

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1. INTRODUCTION.

When a galvanic cell is constructed out of two half cells, the measurable value of the E. M. F. is the algebraic sum of the potential differences of these two single electrodes and the contact potential which develops at the junction of the two unlike solutions. Thus, whenever the necessity occurs to determine the E. M. F. of one of these single electrodes, it is a matter of first importance to know the value of the contact potential. In general, however, it is impossible to determine the value of the contact potential experimentally, because, by nature, it cannot be measured separately. And, so long as the measurement of the contact potential is impossible, the E. M. F. of the single electrode cannot be determined.

In order to remove this difficulty which lies in the course of E. M. F. measurements of single electrodes, many investigators[1] have deduced theoretical expressions for the calculation of the value of a contact potential. But since the use of these expressions is limited to some special cases of the concentration of solutions and the composition of ions, they are of not much avail in practice.

Now, if some method of the conjunction of cells were devised by which no contact potential should develop, the above stated difficulty

1 W. Nernst, Zs. physik. Chem., **2**, 613 (1888); *Ibid.*, **4**, 129 (1889); M. Planck, Wied. Ann., **40**, 561 (1890); P. Henderson, Zs. physik. Chem., **59**, 118 (1907); *Ibid.*, 63, 325 (1908); G. N. Lewis and L. W. Sargent, J. Amer. Chem. Soc., **31**, 363 (1909).

would be swept away. An important guide to the devise of such method of conjunction was given by the theory of W. Nernst[1], that the contact potential is due to the unequal migration of ions, and on his suggestion, S. Bugarszky[2] devised the following method: if an electrolyte, for example potassium nitrate, is added in high and uniform concentration throughout the entire cell, the current in the cell is carried mainly by the added electrolyte, so that the measurable E. M. F. consists only of the electrode potential differences of the two single electrodes. This is a very appropriate devise for the purpose of eliminating the contact potential. But as the addition of such an electrolyte would bring about some changes in the properties of the original electrode solutions, it is not always a sound method in experimental works.

Another method of eliminating a contact potential, devised by O. F. Tower[3], consists in the interposition of concentrated ammonium nitrate or potassium chloride solution at the junction of the two electrode solutions. This method has been pursued by many investigators. A. C. Cumming[4] used concentrated solutions of potassium nitrate, ammonium nitrate, or potassium chloride as the connecting solution of the cells of the following type:

$$Hg|Hg_2Cl_2|1\ N.\ HCl—0{\cdot}1\ N.\ HCl|Hg_2Cl_2|Hg$$

$$Hg|Hg_2Cl_2|1\ N.\ LiCl—0{\cdot}1\ N.\ LiCl|Hg_2Cl_2|Hg.$$

He concluded that a concentrated ammonium nitrate solution brought the best result. R. Abegg and A. C. Cumming[5] also found that the ammonium nitrate solution interposed between the two electrode solutions gives a satisfactory result in the case of silver nitrate concentration cells. N. Bjerrum[6] who used a potassium chloride solution

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1 *Loc. cit.*
2 Zs. anorg. Chem., **14**, 145 (1897)
3 Zs. physik. Chem., **20**, 198 (1896).
4 Trans. Faraday Soc., **2**, 213 (1906).
5 Zs. Elektrochem., **13**, 18 (1907).
6 Zs. physik. Chem., **53**, 428 (1905); Zs. Elektrochem., **17**, 58, (1911); *Ibid.*, **17**, 389 (1911).

of various concentrations as a connecting solution, concluded that a saturated potassium chloride solution eliminates not all the contact potentials. He deduced an empirical rule which has thenceforth been adopted in general in the investigation of the physiological solutions; that is, when the saturated and half-saturated solutions of potassium chloride are used as the connecting solution in succession, and if there be no difference in the E. M. F. between them, then the elimination of the contact potential is complete. But if there be a difference, it is equal to the amount of the contact potential still unremoved.

At the present day, following the suggestion of W. Ostwald,[1] it is customary to use a concentrated potassium chloride solution as the connecting solution in almost all investigations of galvanic cells, and it is generally considered that the contact potential can be eliminated in this way. And in fact the elimination seems almost complete when the electrode solutions are very dilute.

The mechanism of the elimination is, however, quite obscure, and we can only say that the concentrated solution of ammonium nitrate or of potassium chloride has the property of eliminating the contact potential. But as the solutions, which are recognized to be effective for the elimination of the contact potenial, are concentrated solutions of potassium chloride or of ammonium nitrate, we may draw the following conclusion: a salt solution by which the contact potential is completely eliminated, must possess the following conditions:

1) Equal mobilities of the cation and anion.
2) The high solubility of the salt, namely, its concentration be far greater than that of electrode solutions.

Potassium chloride nearly fulfils the first condition, and ammonium nitrate the second.

On the other hand, H. A. Fales and W. C. Vosburgh[2] determined

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1 Ostwald und Luther, Physiko-chemische Messungen, 2. Auf., S. 386.

2 J. Amer. Chem. Soc., 40, 1291 (1918).

the values of several important single electrodes and contact potentials on the following assumptions :

1) The value of the contact potential which develops at the junction of 1 N. KCl and 4•1 N., 3•5 N., 2•5 N., 1•75 N., or 0•1 N. KCl, is correctly expressed by Nernst's formula :

$$E = RT\frac{u-v}{u+v}log\frac{C_1}{C_2}$$

2) In the cell of the type

$$Hg|Hg_2Cl_2|x\ N.\ HCl—x\ N.\ HCl|H_2(1\ Atmos.),$$

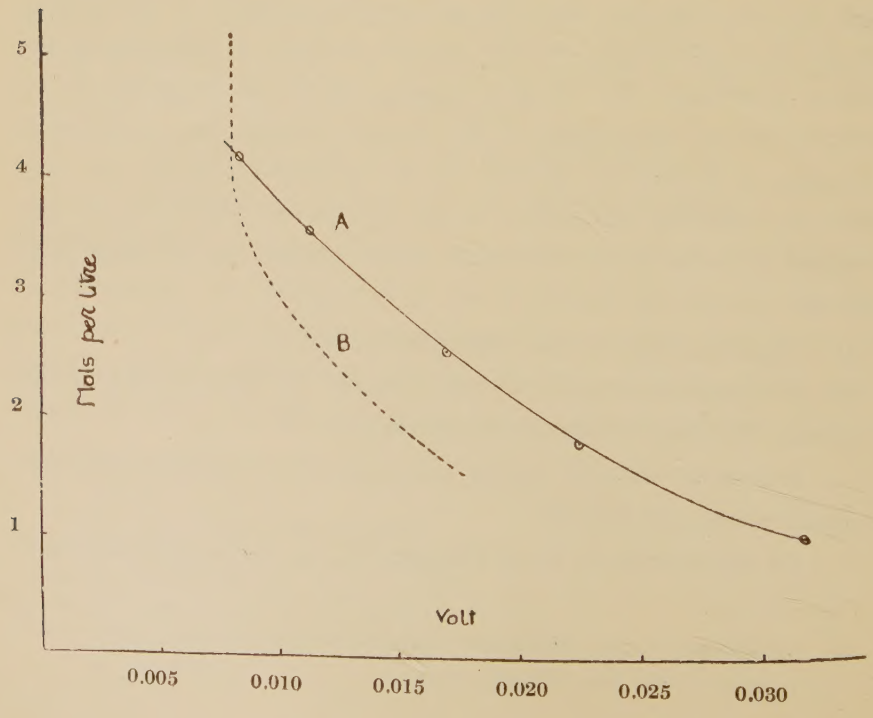
as x is varied, the electrode potential difference at each electrode changes by the same amount, but in the opposite direction.

Among their investigations there is a series of experiments in which the combination of the type

$$Hg|Hg_2Cl_2|1\ N.\ KCl—1\ N.\ HCl|Hg_2Cl_2|Hg$$

was studied with the interposition of potassium chloride solutions of various concentrations. If we plot the result referring to a rectangular

Fig. 1



coordinate, taking the measured E. M. F. as the abcissa and the concentration of potassium chloride as the ordinate, we obtain the curve A as shown in Fig. 1. According to Fales and Vosburgh, when 4·1 N. KCl is used as a connecting solution, the result is as follows:

$$\underset{}{\mathrm{Hg}|\mathrm{Hg_2Cl_2}|}\ \underset{\leftarrow}{1\text{ N. KCl}}\ \underset{0\cdot5648}{}\ \underset{\leftarrow}{4\cdot1\text{ N. KCl}}\ \underset{0\cdot0002}{}\ \underset{}{\text{—1 N. HCl}|\mathrm{Hg_2Cl_2}|\mathrm{Hg}}$$

none $\quad 0\cdot5567$

and the observed E. M. F. = 0·0083.

As far as the result is concerned the elimination is almost complete. If, however, the potassium chloride solution only is active in the elimination, the value of the E. M. F. of the cell must remain constant before and behind the concentration of 4·1 N. In other words, the curve must become gradually parallel to the axis of the ordinate before the concentration reaches 4·1 N., as is diagrammatically shown by the curve B.

As to the connecting solution, the more concentrated it is, compared with the electrode solutions, the better seems to be the elimination, and then, if once the contact potential has been eliminated at a certain concentration, no change will take place on the E. M. F. of the cell by further increase of the concentration. If this consideration is justified, no existence of the contact potential at the junction, 4·1 N. KCl—1 N. HCl, must be due to the accidental fact that the curves A and B intersect each other at the point where the concentration of potassium chloride is 4·1 N.

Looking over the literature of cells, it can be inferred that in case of a comparatively high concentration of electrode solutions, it is especially necessary to use a still more concentrated one as the connecting solution. Moreover, as has been stated above, it is desirable to use a salt solution in which the mobilities of the cation and anion are equal.

On the suggestion of Prof. Y. Osaka, the author took up the present investigation to study this problem under the above-stated consideration.

For the cell, the following combination was selected.

$$Hg|Hg_2Cl_2|1\ N.\ KCl—1\ N.\ HCl|Hg_2Cl_2|Hg.$$

The reasons why such combination was selected are three.

1) If electrode solutions were more dilute, as the elimination of the contact potential might be practically complete by a concentrated solution of potassium chloride, we will not be able to know the advantage of using the special connecting solution.

2) The potassium chloride-calomel cell is one of the best known electrodes of its nature.

3) The hydrochloric acid-calomel cell, which contains an electrolyte with ions of very different mobilities, would develop a great contact potential. So it would be advantageous for comparing various connecting solutions.

2. EXPERIMENTAL.

Apparatus for E. M. F. Measurement.

All measurements were carried out in an oil thermostat at 25·0°C. The oil used in the thermostat was a transparent machine oil with a boiling point of about 290°C. The E. M. F. was determined by the zero-method with a Leeds and Northrup potentiometer and a D'Arsonval galvanometer.

Standard Cell.

In the preparation of cadmium elements, special attention must be paid to the quality of the mercurous sulphate. According to G. A. Hulett[1], the best mercurous sulphate is obtained by electrolysis of sulphuric acid (6 : 1) with a current density of 0·5 amp., using platinum as the catho le and mercury as the anode. The product is then washed with a saturated cadmium sulphate solution until no trace of acid can be detected.

Two cadmium elements which were made up of the mercurous sulphate thus prepared, are designated as No. 1 and No. 2. For the

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[1] Zs. physik. Chem., **49**, 483 (1904).

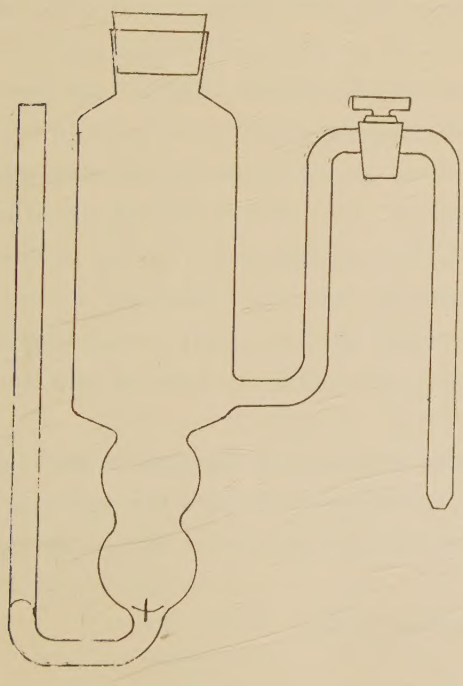
purpose of comparison four more cadmium elements were made up, two of which were prepared with mercurous sulphate of Merck (No. 3 and No. 4) and the other two with the ordinary commercial stuff (No. 5 and No. 6).

The following table represents the values of these cadmium elements compared with Fritz Köhler Weston normal element No. 325 (0•10183 volt).

Number of element	Measured soon after preparation	Measured after two months
1	1•01825	1•01825
2	1•01827	1•01827
3	1•01895	1•01835
4	1•01890	1•01857
5	1•0262	1•0268
6	1•0269	1•0271

From this table it may be seen that elements made up of electrolytically prepared mercurous sulphate bring the best result.

Fig. 2



Calomel Electrode.

Fig. 2 shows the form of calomel cell used. The abvantages of this form of cell are: 1) the form is comparatively simple and it does not need a great quantity of calomel and mercury; 2) the electrode solution can simlpy be poured into or out of the cell without disturbing the platinum electrode immersed in the mercury.

Though in the ordinary case the cock of the calomel cell is left ungreased, the author, according to W. M.

Clark,[1] obtained a good result by greasing the narrow part of the socket and the wide part of the key to make it turn easily and to prevent the creeping out of the salt.

All vessels as well as the calomel cell, used in the experiments, were treated successively with a chromic acid mixture for three days, a strong solution of potassium hydroxide for a day, a nitric acid for twelve hours, and finally washed thoroughly with water.

Materials.

Normal hydrochloric acid solution :— Redistilled hydrochloric acid was diluted to a proper degree and standardized with sodium carbonate of Merck. Its concentration was such that, according to Prof. Y. Osaka,[2] it becomes just one normal at 25°C. All the other standard solutions were prepared in the same way.

Normal potassium chloride solution :— Potassium chloride recrystallized three times was fused in a platinum crucible and the proper quantity of it was dissolved.

Potassium nitrate :— After a recrystallization, it was dried at 160°C.

Lithium chloride :— Commercial lithium chloride was precipitated as lithium carbonate. It was then dissolved in pure hydrochloric acid, and as much as possible of the excess of the acid was expelled on a water bath. When it was cooled, lithium chloride crystallized out. These crystals, after being separated from the mother liquor by means of a centrifugal separator, were again dissolved in water. It was again evaporated and cooled—such treatment was repeated several times, and finally a lithium chloride containing no trace of acid was obtained.

Calomel :— Freshly distilled mercury was dissolved in distilled nitric acid of specific gravity 1•2, an excess of mercury being present, then the solution was diluted and it was poured into a dilute solution

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[1] The Determination of Hydrogen Ions, p. 131.

[2] These Memoirs, **4**, 113 (1920).

of distilled hydrochloric acid. The precipitated calomel was well washed with water by successive decantations, then with that solution with which it was to be used in a calomel cell. Finally it was shaken with the same solution in a shaking machine for two days.

Connecting Solutions.

As has already been pointed out, it is most desirable to use, as the connecting solution, a very concentrated solution of a salt having a cation and an anion the mobilities of which are just equal. Now, as the connecting solution of the first kind, a mixed solution of potassium chloride and potassium nitrate was selected ; the mobilities of the ions which are contained in this mixed solution at 25°C. are as follows :

$$K^{\cdot}\ 74{\cdot}63 \qquad Cl'\ 75{\cdot}50 \qquad NO_3'\ 70{\cdot}70$$

Now let x be the percentage of the chlorine ion of the whole anion, then for the solution in which the average value of the mobilities of the anions is equal to the mobility of the cation, we have

$$74{\cdot}63 \times 100 = 75{\cdot}50x + 70{\cdot}70(100 - x)$$

By solving the equation we have for the percentages of the two salts

$$KCl : KNO_3 = 81{\cdot}87 \text{ mols} : 18{\cdot}13 \text{ mols.}$$

The mixed solution of this proportion used in the present investigation were as follows :

No. 1.	KCl	3·848	mols per litre.
	KNO_3	0·852	
No. 2.	KCl	2·574	,, ,, ,,
	KNO_3	0·568	
No. 3.	KCl	1·283	,, ,, ,,
	KNO_3	0·284	

The connecting solution of the second kind was a mixed solution of ammonium nitrate and lithium chloride. Their propotion was calculated in the same way as in the case of the first kind. The mobilities of the ions are

$$Li^{\cdot}\ 39{\cdot}78 \qquad NH_4^{\cdot}\ 74{\cdot}70 \qquad Cl'\ 75{\cdot}50$$
$$NO_3'\ 70{\cdot}70$$

Let x be the percentage of the ammonium ion of the whole cation, or that of the nitrate ion of the whole anion, then

$$74{\cdot}70x + 39{\cdot}78(100-x) = 75{\cdot}50(100-x) + 70{\cdot}70x$$

By the determination of x, the required proportion will be obtained, which is

$$NH_4NO_3 : LiCl = 89{\cdot}93 \text{ mols} : 10{\cdot}07 \text{ mols.}$$

Of the solution of this kind, a solution of comparatively higher concentration can be obtained. The solutions used in the present investigation were

No. 4.	NH_4NO_3	8·39	mols per litre.
	LiCl	0·94	
No. 5.	NH_4NO_3	5·59	,, ,, ,,
	LiCl	0·63	
No. 6.	NH_4NO_3	4·20	,, ,, ,,
	LiCl	0·47	
No. 7.	NH_4NO_3	2·10	,, ,, ,,
	LiCl	0·24	

In the above calculations it was assumed that as all the salts concerned were uni-uni binary, they dissociate in a mixed solution to the same degree.

Method of Junction.

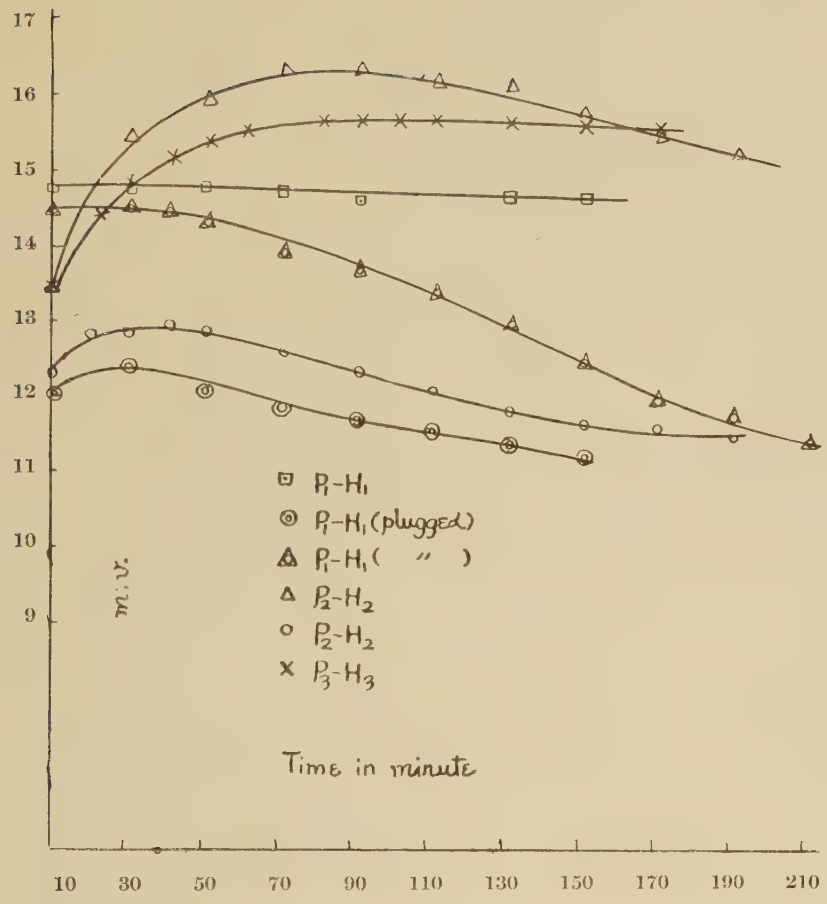
One of the greatest difficulties which we encounter in the course of E. M. F. determinetion of a galvanic cell with contact potentials is the time effect, that is, the variation of the E. M. F. due to lapse of time. This variation comes from the concentration change of the solutions at their junctions owing to the mechanical mixing and the diffusion which take place at the interface of the two solutions. In the combination of the cells which were used in the present investigation, this effect was considerable.

Fig. 3 shows how the E. M. F. varies with the time in the combination of the type

$$Hg|Hg_2Cl_2|1 \text{ N. KCl}—3{\cdot}5 \text{ N. KCl}—1 \text{ N. HCl}|Hg_2Cl_2|Hg,$$

where P and H denote calomel cells of 1 N. KCl and 1 N. HCl

Fig. 3



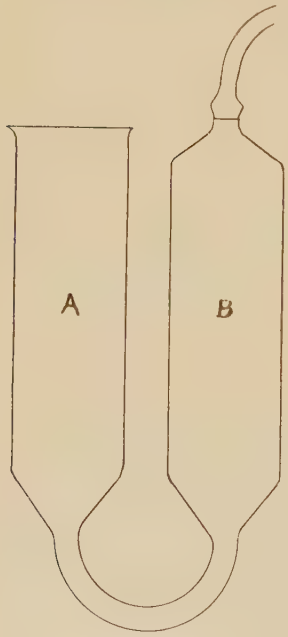
respectively. The first measurement of E. M. F. was taken at exactly ten minutes after the moment when the junctions were made by dipping the side tubes of the component cells into the 3·5 N. potassium chloride solution contained in a small beaker, and successive observations were made every ten or twenty minutes.

This diagram shows that the time effects are very different from one another even when the same electrodes were used. And it may also be seen from it that though the ends of the side tubes were plugged with wooden cones to prevent as far as possible the mechanical flow,

the time effect is still different in each measurement. Clark,[1] in his book, pointed out the necessity of recording the time elapsing after the formation of the liquid junction as a part of the data of the E. M. F., but the above experiments show that such record seems to be of no practical use for finding the true value.

To get around these difficulties there have been several attempts to make a reproducible liquid junction by preventing the mechanical mixing and diffusion. One of the simplest devises is the sandfilling method of Bjerrum,[2] but it seems it does not always give a satisfactory result. The best devise both in theory and in practice is the method of making a sharp boundary at the interface of the two unlike solutions. G. N. Lewis and F. F. Rupert,[3] Lewis, Brighton and Sebastian,[4] and A. B. Lamb and A. T. Larson[5] devised clever methods which are found to be much more reproducible than the junctions usually made, but these methods seem to be somewhat too complicated for general use.

Fig. 4



In the present experiment, a connecting vessel as shown in Fig. 4 was used. At first, the connecting solution is sucked up into the tube B and the side tubes of the component cells are introduced into the tube A to the same level. After the apparatus has attained the temperature of 25° C., the pinch cock on the rubber tubing is opened and the connecting solution is al-

1 *Loc. cit.*

2 Bjerrum, *Loc. cit.* ; G. N. Lewis, T. B. Brighton and R. L. Sebastian, J. Amer. Chem. Soc., **39**, 3245 (1917); C. N. Myers and S. F. Acree, Amer. Chem. J., **50**, 396 (1913).

3 J. Amer. Chem. Soc., **33**, 299 (1911).

4 *Loc. cit.*

5 J. Amer. Chem. Soc., **42**, 229 (1920).

lowed to rise slowly in A. Taking the moment when the side tubes come in contact with connecting solution as the starting point, successive observations are made as quickly as possible. The data obtained in this way are plotted on a time-E. M. F. diagram and the curve obtained by connecting these points is extended and the point of intersection of this curve and the E. M. F. -axis is sought for. This point may represent the E. M. F. at the moment of contact.

The reasons why such a method was used are as follows: as the influence of the diffusion on the E. M. F. may be traced by a very smooth curve on the time-E. M. F. diagram, if the utmost care is taken to prevent the mechanical mixing, we should be able to eliminate the diffusion effect by means of this method. Moreover, even if a mechanical mixing occurs more or less at first, as the mixed boundary, by nature, becomes the diffused boundary in course of time, by this method we should also be able to reduce the mechanical mixing effect.

An example of the results obtained by means of this method is given in the following table:

$Hg \mid Hg_2Cl_2 \mid$ 1 N. KCl (P_1 —3·5 N. KCl—1 N. HCl $\mid Hg_2Cl_2 \mid Hg(H_1)$	
Time elapsing after making the contact	E. M. F. (volt)
The first measurement.	
m s	
0 20	0·0121
1 40	0·01245
2 40	0·0129
3 30	0·0132
4 20	0·0134
5 00	0·0136
6 20	0·0137
7 30	0·0139
9 00	0·0141
The second measurement.	
m s	
0 30	0·0115
1 40	0·0120
2 30	0·0124
3 40	0·01275
4 50	0·0129
5 40	0·0130
6 20	0·0131
7 50	0·01325
8 40	0·0133

Hg | Hg_2Cl_2	1 N. KCl (P_1)—3·5 N. KCl—1 N. HCl	Hg_2Cl_2 | Hg' (H_1)
Time elapsing after making the contact	E. M. F. (volt)	

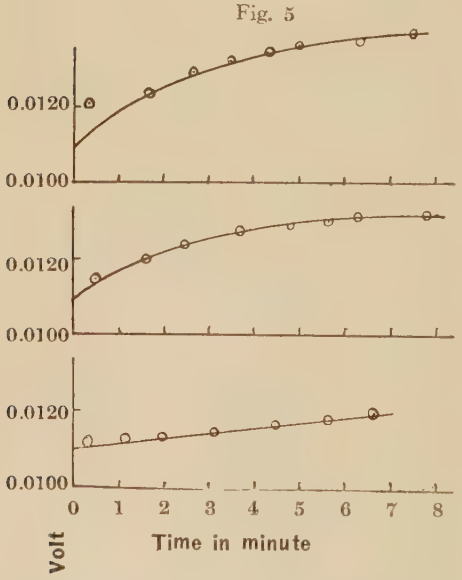
The third measurement.

m	s	
0	20	0·0112
1	10	0·0113
2	00	0·0113
3	10	0·01145
4	30	0·01165
5	40	0·0118
6	40	0·01195

From these data, the required E. M. F. may be obtained graphically as shown in Fig. 5. The mean value thus found is 0·0110 ± 0·00000 volt.

In the following experiment this method of forming a junction was used. By means of this method, however, we cannot always expect such a fair coincidence of the results as above cited. For example, the following data were obtained in the measurement of the combination P_1—H_3.

Fig. 5



0·0108
0·0112
0·0111
0·0113

Such inconstancy in data may spring from the following facts:

1) We are often uncertain two or three seconds in the determination of the starting point—the moment of contact. When the inclination of the curve is small against the horizontal axis, the error will be negligible, but when the inclination is large, the error will be more or less appreciable.

2) Though the utmost care is taken in making the liquid junction, more or less mechanical mixing is unavoidable. As has keen

already stated, the mixed boundary becomes the diffused boundary in course of time, so the data of the initial part of the measurement—the part affected by the mixed boundary—were discarded. This effect of mixed boundary seems to cease within one minute when two solutions are brought together very gently. In some cases, however, it is very difficult to determine to what extent we may discard the data.

3) Calomel cells, when repeatedly used, produce polarization and give inconstant results ; for example the results of the successive measurements of the combination P_1—H_3 are

0•0108,
0•0119,
0•0125.

According to the author's experience, a calomel cell once used must be let stand for an hour at least.

Preliminary experiment.

To examine the reproducibility of the contact potential at the liquid junction, a combination of the type

[1]$Hg|Hg_2Cl_2|1$ N. KCl—3•5 N. KCl—1 N. HCl$|Hg_2Cl_2|Hg$

was measured. The results are represented in the following table. Each datum is the mean value of three or four measurements.

calomel cells used	E. M. F.
P_1—H_1	0•0110
P_1—H_2	0•0111
P_1—H_3	0•0111
P_2—H_1	0•0111
P_2—H_2	0•0113
P_2—H_3	0•0110
P_3—H_1	0•0115
P_3—H_3	0•0115
Mean	0•0112±0•00021

The result of this cell obtained by Fales and Vosburgh is 0•0114 volt.

[1] The positive current runs through the cell from right to left. This applies to the corresponding parts in the following.

3. RESULTS.

Experiment 1.

Hg | Hg_2Cl_2 | 1 N. KCl—No. 1— 1 N. HCl | Hg_2Cl_2 | Hg	
calomel cells used	E. M. F.
P_1—H_1	0·0064
P_1—H_2	0·0063
P_1—H_3	0·0061
P_2—H_1	0·0068
P_2—H_2	0·0062
P_2—H_3	0·0069
P_3—H_1	0·0068
P_3—H_2	0·0062
P_3—H_3	0·0070
mean	0·0065±0·00035

Experiment 2.

Hg | Hg_2Cl_2 | 1 N. KCl—No. 2— 1 N. HCl | Hg_2Cl_2 | Hg	
calomel cells used	E. M. F.
P_1—H_1	0·0128
P_1—H_2	0·0129
P_1—H_3	0·0127
P_2—H_1	0·0137
P_2—H_2	0·0128
P_2—H_3	0·0137
P_3—H_1	0·0135
P_3—H_2	0·0125
P_3—H_3	0·0135
mean	0·0131±0·00047

Experiment 3.

Hg | Hg_2Cl_2 | 1 N. KCl—No. 3— 1 N. HCl | Hg_2Cl_2 | Hg	
calomel cells used	E. M. F.
P_1—H_1	0·0257
P_1—H_2	0·0257
P_1—H_3	0·0258
P_2—H_1	0·0265
P_2—H_2	0·0261
P_2—H_3	0·0263
P_3—H_1	0·0255
P_3—H_2	0·0251
mean	0·0258±0·00045

Experiment 4.

Hg | Hg_2Cl_2 | 1 N. HCl – No. 4 — 1 N. KCl | Hg_2Cl_2 | Hg	
calomel cells used	E. M. F.
P_1—H_1	0·0031
P_1—H_2	0·0029
P_1—H_3	0·0026
P_2—H_1	0·0023
P_2—H_2	0·0029
P_3—H_1	0·0021
P_3—H_2	0·0022
mean	0·0026 ± 0·00039

Experiment 5.

Hg | Hg_2Cl_2 | 1 N. KCl—No. 5— 1 N. HCl | Hg_2Cl_2 | Hg	
calomel cells used	E. M. F.
P_1—H_1	0·0028
P_1—H_2	0·0028
P_2—H_2	0·0032
P_2—H_3	0·0030
P_3—H_1	0·0027
P_3—H_3	0·0031
mean	0·0029 ± 0·00020

Experiment 6.

Hg | Hg_2Cl_2 | 1 N. KCl—No. 6— 1 N. HCl | Hg_2Cl_2 | Hg	
calomel cells used	E. M. F.
P_1—H_1	0·0086
P_1—H_2	0·0093
P_2—H_2	0·0087
P_2—H_3	0·0087
P_3—H_2	0·0090
P_3—H_3	0·0087
mean	0·0088 ± 0·00027

Experiment 7.

Hg | Hg_2Cl_2 | 1 N. KCl–No. 7–1 N. HCl | Hg_2Cl_2 | Hg	
calomel cells used	E. M. F.
P_1-H_1	0·0201
P_1-H_2	0·0205
P_2-H_2	0·0208
P_2-H_3	0·0206
P_3-H_1	0·0209
P_3-H_3	0·0209
mean	0·0205±0·00034

Experiment 8.

Hg | Hg_2Cl_2 | 1 N. KCl–8·39 N. NH_4NO_3–1 N. HCl | Hg_2Cl_2 | Hg	
calomel cells used	E. M. F.
P_1-H_1	0·0013
P_1-H_2	0·0021
P_2-H_1	0·0019
P_2-H_2	0·0016
P_2-H_3	0·0019
P_3-H_1	0·0021
P_3-H_3	0·0018
mean	0·0018±0·00029

Experiment 9.

Hg | Hg_2Cl_2 | 1 N. KCl–6·29 N. NH_4NO_3–1 N. HCl | Hg_2Cl_2 | Hg	
calomel cells used	E. M. F.
P_1-H_1	0·061
P_2-H_2	0·057
P_2-H_3	0·062
P_3-H_1	0·061
P_3-H_3	0·059
mean	0·060±0·00020

The symbols a and b in the following tables denote 1/10 N. $ZnCl_2$ calomel cell and 1/100 N. $ZnCl_2$ calomel cell respectively.

Experiment 10.

Hg | Hg_2Cl_2 | N/100. $ZnCl_2$—3·5 N.KCl—N/10. $ZnCl_2$ | Hg_2Cl_2 | Hg	
calomel cells used	E. M. E.
a_1—b_1	0·0546
a_2—b_2	0·0555
a_3—b_3	0·0548
mean	0·0550

Experiment 11.

Hg | Hg_2Cl_2 | N/100. $ZnCl_2$—4·1 N.KCl—N/10. $ZnCl_2$ | Hg_2Cl_2 | Hg	
calomel cells used	E. M. E.
a_1—b_1	0·0553
a_1—b_2	0·0554
a_2—b_1	0·0557
a_2—b_2	0·0559
a_2—b_3	0·0558
a_3—b_2	0·0557
a_3—b_3	0·0557
mean	0·0556±0·00022

Experiment 12.

Hg | Hg_2Cl_2 | N/100. $ZnCl_2$—No. 1—N/10. $ZnCl_2$ | Hg_2Cl_2 | Hg	
calomel cells used	E. M. E.
a_1—b_1	0·0545
a_1—b_2	0·0549
a_1—b_3	0·0552
a_2—b_1	0·0547
a_2—b_2	0·0545
a_2—b_3	0·0550
a_3—b_1	0·0546
a_3—b_2	0·0543
a_3—b_3	0·0546
mean	0·0547±0·00028

Experiment 13.

Hg | Hg_2Cl_2	N/100. $ZnCl_2$—10·18 N. NH_4NO_3 · N/10. $ZnCl_2$	Hg_2Cl_2 | Hg
calomel cells used	E. M. E.	
a_1—b_1	0·0551	
a_1—b_2	0·0539	
a_1—b_3	0·0550	
a_2—b_1	0·0544	
a_2—b_2	0·0541	
a_2—b_3	0·0544	
a_3—b_1	0·0547	
a_3—b_2	0·0540	
a_3—b_3	0·0543	
mean	0·0544±0·00042	

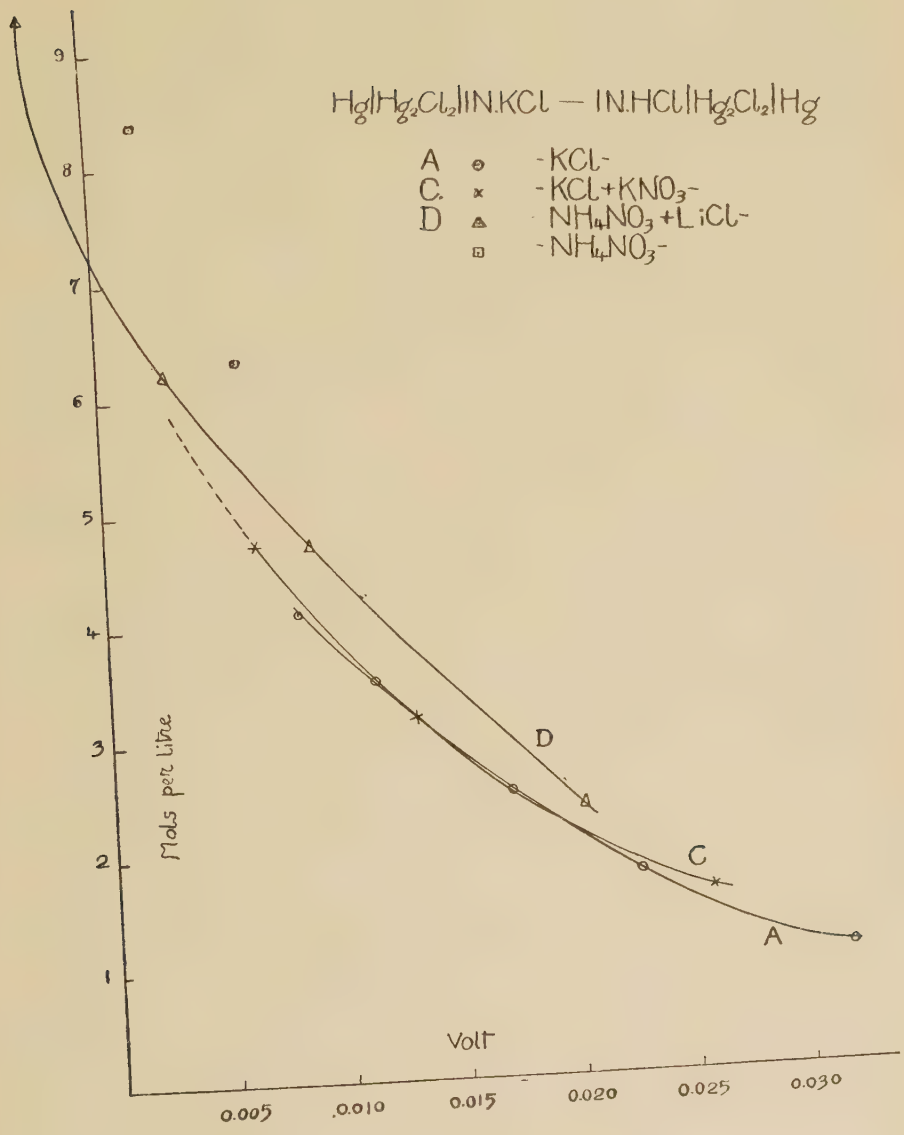
Expe iment 14.

Hg | Hg_2Cl_2	N/100. $ZnCl_2$—6·72 N. NH_4NO_3—N/10. $ZnCl_2$	Hg_2Cl_2 | Hg
calomel cells used	E. M. E.	
a_1—b_1	0·0553	
a_1—b_2	0·0540	
a_1—b_3	0·0546	
a_2—b_1	0·0545	
a_2—b_2	0·0540	
a_2—b_3	0·0545	
a_3—b_1	0·0547	
a_3—b_2	0·0539	
a_3—b_3	0·0544	
mean	0·0544±0·00044	

Experiment 15.

Hg | Hg_2Cl_2	N/100. $ZnCl_2$—No.4—N/10. $ZnCl_2$	Hg_2Cl_2 | Hg
calomel cells used	E. M. E.	
a_1—b_1	0·0550	
a_1—b_2	0·0542	
a_1—b_3	0·0547	
a_2—b_1	0·0544	
a_2—b_2	0·0543	
a_2—b_3	0·0547	
a_3—b_1	0·0547	
a_3—b_2	0·0540	
a_3—b_3	0·0546	
mean	0·0545±0·0003	

Fig. 6


Hg|Hg2Cl2|IN.KCl — IN.HCl|Hg2Cl2|Hg
A -KCl-
C. -KCl+KNO3-
D -NH4NO3+LiCl-
-NH4NO3-
Mols per Litre
Volt
D
C
A
0.005
0.010
0.015
0.020
0.025
0.030

4. DISCUSSION OF RESULTS.

The results of experiments (from 1 to 9) are represented graphically in Fig. 6. In this figure the results achieved by Fales and Vosburgh, in which potassium chloride solutions were used as the connecting solution, are also added.

It was expected at first that if the connecting solution used in the present experiment were ideal, the curve C and D would begin to become parallel to the ordinate at a certain concentration of the connecting solution, and if the values of the half cells, 1 N. $KCl|Hg_2Cl_2|Hg$ and 1 N. $HCl|Hg_2Cl_2|Hg$, were 0·5648 and 0·5567 respectively, the value of the parallel part of the curve would be epual to the difference between the values of these two half cells, namely, 0·0081 volt.

But the result as represented in the figure shows that though the curve C has a slightly greater tendency to be parallel to the ordinate at the upper part than the curve A, the difference caused by the addition of potassium nitrate to potassium chloride is almost negligible. The concentration of the first kind of connecting solution is insufficient for this cell.

As the second kind of connecting solution can be prepared in a more concentrated solution than potassium chloride solution or the first kind of connecting solution, the author expected some good results from it for the present purpose. The curve D is prone to be parallel to the ordinate gradually as the connecting solution is more concentrated, and may be quite parallel to it at about −0·0025— −0·003 volt. (Pure ammonium nitrate solution shows a different result from the second connecting solution as shown in this figure.)

From the curve D it may be seen that if the consideration which has already been stated at the introduction,—that once the contact potential has been eliminated at a certain concentration of the connecting solution, no change will take place on the E. M. F. of the cell, when the concentration is further increased—is justified, the value of

the cell in the present investigation which does not contain the contact potential is −0•0025— −0•0030 volt. This value was determined by Fales and Vosburgh to be 0•0081 volt.

The correctness of the value of Fales and Vosburgh depends on their conclusion that the contact potential at the junction, 4•1 N. KCl— 1 N. HCl, is null, and on the values of the calomel cells which they adopted. As to the values of the calomel cells, the author has no materials to discuss now, but as to the conclusion that the contact potential at the junction, 4•1 N.KCl— 1 N. HCl, is null, the author hesitates to accept it from consideration of Nernst's theory of the contact potential. The author, therefore, concludes from the above consideration that the value containing no contact potential of this cell is −0•0025— −0•0030.

Accordingly the second kind of connecting solution at a comparatively higher concentration is satisfactory for the cell above considered.

Though the author expected the coincidence of the curves C and D, the results were somewhat different. It might come from the error in the assumption that the salts dissociate in the solution in the same degree. But from Fig. 6, it may be expected that if it were possible to prepare the more concentrated solution of the first kind of solution, the curve C would coincide with the curve D after all.

If we use the electrode solution, of which the difference of mobilities between the cation and anion is not so great, and which is comparatively dilute, the cell gives the constant value within 1 m. v., using ammonium nitrate, potassium chloride, the first kind of solution or the second kind of solution over a certain concentration, as shown by the experiments (from 10 to 15). In such case, when we use the concentrated solution of potassium chloride or of ammonium nitrate as the connecting solution, we need not use a special solution owing to the perfect elimination of contact potential.

In conclusion, the author wishes to express his sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind guidance.

On the Equilibrium of the System : Ferric Chloride, Aniline Hydrochloride, Hydrogen Chloride and Water at 25·0°.

By

Yukichi Osaka, Goro Shima and Ryohei Yoshida.

(Received July 11, 1923)

R. M. McKenzie[1] obtained some double halides of iron and some aromatic bases, of which those of aniline hydrochloride were the following ;

$FeCl_3.\ 2C_6H_5NH_3Cl$, $FeCl_3.\ 2C_6H_5NH_3Cl.H_2O$,
$FeCl_3.\ 6C_6H_5NH_3CI$, and $FeCl_3.\ 6C_6H_5NH_3Cl.2H_2O$.

All his attempts to make quantitative determinations of the water of crystallisation in these salts were unsuccessful and the formulas of the double salts, both anhydrous and hydrated, were calculated from the quantitative determinations of the chlorine and iron.

This work suggested that it might be of some interest to study the system consisting of ferric chloride, aniline hydrochloride, hydrogen chloride and water from the standpoint of the phase theory. The experimental work was first undertaken by G. Shima and then continued by R. Yoshida. The following are the results so far obtained.

MATERIALS.

Aniline hydrochloride. Pure aniline from E. Merck was distilled and then redistilled under reduced pressure. The aniline thus prepared was mixed with an equivalent quantity of redistilled hydrochloric acid

1 Amer. Chem. J., **50**, 309 (1913).

in a porcelain beaker externally cooled and the aniline hydrochloride, which crystallised out, was preserved in a desiccator over sulphuric acid.

Ferric chloride. The purest preparation of E. Merck was used without further purification.

Hydrochloric acid. A twenty per cent solution was prepared by distillation from the acid of Jap. Pharm.

Water. Ordinary distilled water was used.

PROCEDURE.

Proper quantities of ferric chloride and aniline hydrochloride together with some hydrochloric acid were put in an Erlenmeyer flask of about 30 cc. capacity. It was stoppered with a paraffined cork, which was tightly covered with a sheet of oiled paper, and was made to rotate in a thermostat at 25•0° for a few days. Then the liquid phase and residue, more or less wetted with the mother liquor, were subjected separately to analysis.

When the concentration of ferric chloride is high, aniline is oxidised unless the hydrochloric acid is concentrated, and when the hydrochloric acid is concentrated the solubility of the ferric chloride is very great. Under such circumstances the cases where the ferric chloride is very concentrated, could not be studied.

METHODS OF ANALYSIS.

Aniline. It was separated from a weighed sample by decomposition with caustic potash and steam distillation. It was then titrated with a standard solution of bromine with indigo-carmine as indicator.

Iron. To the ferric chloride solution obtained from a weighed sample by driving off the aniline with caustic potash, some potssaium iodide was added and the free iodine thus formed was titrated by sodium thiosulphate with starch as indicator, (G. S.). Or the residue from the distillation of aniline was separated quantitatively by filtration and washing into a solution and solid residue. The solid residue was dissolved in hy-

drochloric acid and the ferric chloride thus formed was reduced to ferrous salt by stannous chloride. The excess of stannous chloride was oxidised by mercuric chloride and with addition of manganous sulphate, phosphoric acid, and sulphuric acid, the ferrous iron was titrated with potassium permanganate, (R. Y.).

Chlorine. The filtrate of the residue from the distillation of aniline was acidified with nitric acid. A known quantity of 1/10 n. silver nitrate was added and its excess was titrated back with a 1/10 n. solution of ammonium thiocyanate with iron alum as indicator.

Water. It was estimated by difference.

RESULTS.

The results are given in the following two tables. In these tables the compositions of the solutions and residues are represented in weight percentages.

TABLE 1.

(Experiments by G. Shima.)

No.	Solution.				Residue			
	Aniline hydrochloride.	Ferric chloride.	Hydrogen chloride.	Water.	Aniline hydrochloride.	Ferric chloride	Hydrogen chloride.	Water.
1	11·29	0·20	21·20	67·41	69·22	2·45	8·83	19·50
2	12·46	0·49	19·57	67·48	49·94	4·78	12·68	32·60
3	10·77	0·11	21·64	67·48	80·94	2·77	11·78	4·51
4	8·94	1·35	19·41	70·30	36·79	6·91	15·41	40·89
5	7·11	0·69	22·48	69·72	26·24	4·76	17 37	51·63
6	5·85	1·10	23·87	69·18	34·52	7·25	17·35	40·88
7	5·05	1·86	22·03	71 06	23·54	5·42	18·10	52·94
8	4·61	3·01	22·28	70·10	22·33	5·95	18·65	53·07
9	3·99	3·35	23·04	69·62	18·12	5·79	20·49	55·60
10	4·05	3·58	22·35	70·02	28·18	7·47	18·04	46·31
11	5·59	6·37	19 17	68 87	40·51	11·39	13·26	34·84
12	3·44	6·31	22·36	67·89	20·58	8·24	22·21	48·97

TABLE 2.

(Experiments by R. Yoshida.)

No.	Solution.				Residue.			
	Aniline hydrochloride.	Ferric chloride.	Hydrogen chloride.	Water.	Aniline hydrochloride.	Ferric chloride.	Hydrogen chloride.	Water.
1	22·78	0·00	11·08	66·14	95·08	0·00	1·25	3·67
2	20·24	1·29	11·78	66·69	74·71	2·60	3·45	19·24
3	18·09	1·03	13·02	67·86	64·28	5·51	5·00	25·21
4	19·59	1 31	12·08	67·02	89·04	3·00	1·23	6·73
5	17·17	2·82	11·88	68·13	59·81	12·69	4·03	23·47
6	13·81	5·18	11·32	69·69	61·52	14·03	3·04	21·41
7	10·92	8·51	10·82	69·75	57·31	14·42	3·98	24·29
8	8·85	8·83	12·66	70·11	51·11	13·92	4·76	30·21
9	7·06	12 12	11·44	69·38	62·50	16·24	2·56	18·70
10	7·09	14 30	10·21	68 40	34·06	15·87	6·25	43 82
11	5·29	16·06	11·69	66·96	35·90	16·93	6·45	40·72
12	4·49	18·16	11·91	65·44	63·63	17·44	2·94	15·99
13	3·96	19·95	11·49	64·60	50·84	19·13	4·13	25·90
14	3·57	21·50	12·89	62·04	53·14	24·91	4·04	17·91
15	3·45	22·84	11·22	62·49	21·75	21·94	8·83	47·48
16	3·47	23·82	10·21	62·50	17·93	23·23	8·20	50·64
17	2·58	23·36	12·96	61·10	47·87	36·62	2·71	12·80
18	2·10	25·59	12·48	59·83	46·77	35·56	3·11	14·56
19	2·07	26·20	12·53	59·20	55·33	35·75	2·22	6·70
20	1·71	28·61	11·71	57·97	49·90	36·72	2·33	11·05
21	1·35	33·10	10·98	54·57	42·83	37·00	3·35	16·82
22	1·57	35·17	7·22	56·04	43·92	38·06	1·67	16·35
23	1·34	36·24	7·52	54·90	45·80	38·07	2·64	13·49

From the data given in Table 2, if we take the cases in which the percentage of hydrochloric acid is approximately constant and represent the composition excluding the hydrochloric acid, by the formula:

$$100mH_2O,\ x\ C_6H_5NH_3Cl,\ (100\text{-}x)\ FeCl_3$$

we obtain Table 3.

TABLE 3.

No.	Solution.		Residue.	
	x	m	x	m
1	100·00	20·88	100·00	0·28
2	95·16	22 54	97·29	1·80
5	88·39	25·22	85·53	2·41
6	76·96	27·93	84·59	2·12
9	42·17	29·82	82·83	1·78
11	29·20	26·57	72·63	5·92
12	23·62	24·79	82·04	1·48
13	19·90	23·35	76·89	2·82
14	17·19	21·53	72·75	1·76
17	12·13	20·68	62·07	1·19
18	9·32	19·08	62·21	1·39
20	6·98	16·97	62·97	1·00
21	4·86	14·12	59·17	1·67

From the data in Table 3, Fig. 1 was plotted.

Next, we take a regular tetrahedron as the coordinates to represent the equilibrium of the system under consideration and project orthogonally the points in the space to the face of $C_6H_5NH_3Cl$, $FeCl_3$ and H_2O, then in the triangular diagram, we have as the three coordinates the following values :[1]

$$(C_6H_5NH_3Cl)+1/3(HCl),$$

$$(FeCl_3)+1/3(HCl),$$

$$(H_2O)+1/3(HCl),$$

where the chemical formula in brackets denotes the molar percentage of that substance.

From Tables 1 and 2, Tables 4 and 5 were calculated respectively for the new coordinates of the orthogonal projection.

TABLE 4.

No.	Solution.			Residue.		
	$C_6H_5NH_3Cl$	$FeCl_3$	H_2O	$C_6H_5NH_3Cl$	$FeCl_3$	H_2O
1	18·36	7·26	74·48	72 16	5·40	22·44
2	18·99	7·01	74·00	54·17	9·01	36·82
3	17·99	7·32	74·69	84·87	6·69	8·44
4	15·41	7·82	76·77	41·93	12·05	46·02
5	14·60	8·19	77·21	32·03	10·55	57 42
6	13·80	9·06	77·14	40·30	13·04	46 66
7	12·40	9·20	78·40	29·57	11·46	58·97
8	12·04	10·44	77·52	26·55	12·16	59·29
9	11·67	11·03	77·30	24·96	12·62	62·42
10	11·50	11·03	77·47	34·19	13·48	52·33
11	11·98	12·76	75·26	44·93	15·81	39·26
12	10·89	13·77	75·34	27·98	15·64	56·38

[1] F. A. H. Schreinemakers, Zs. physik. Chem., **55**, 563 (1909).

Fig. 1

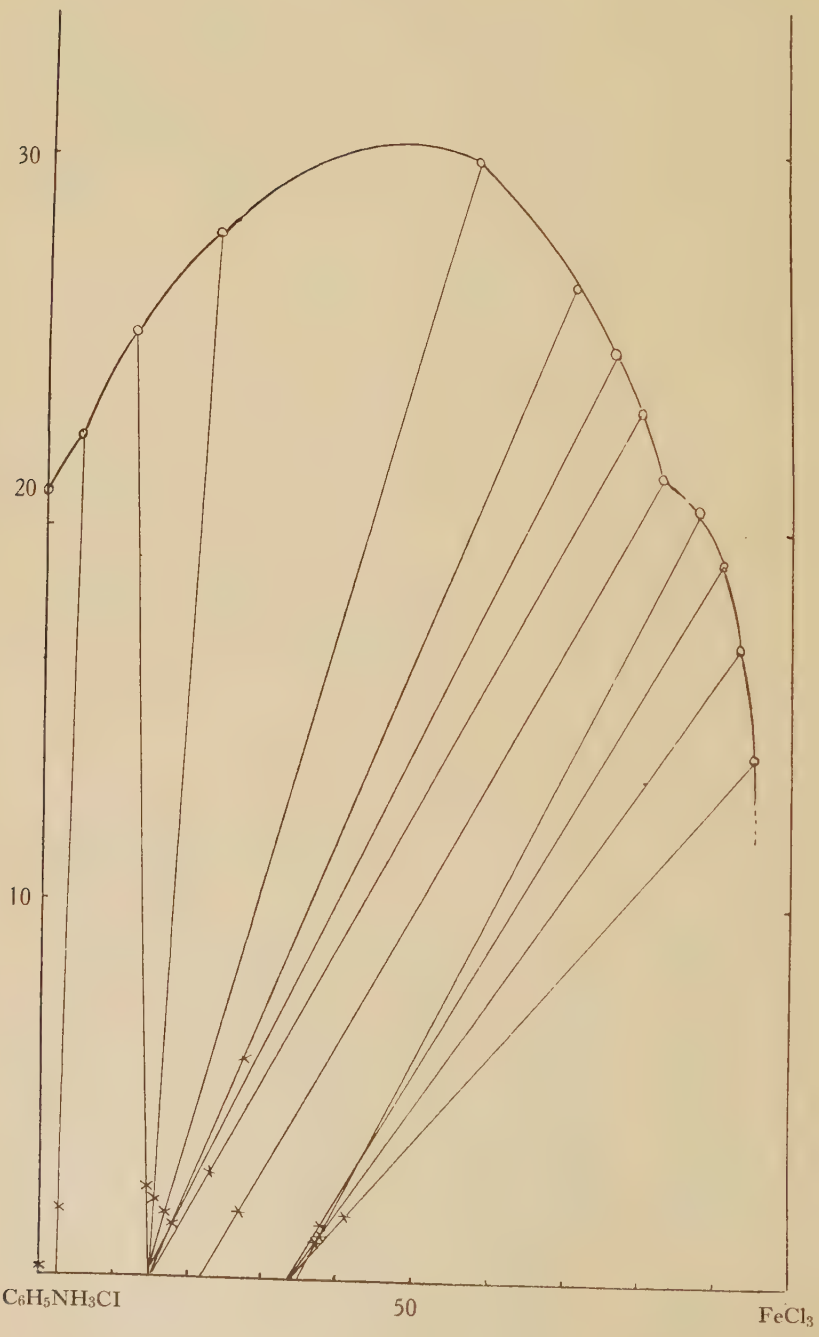


TABLE 5.

No.	Solution.			Resipus,		
	$C_6H_5NH_3Cl$	$FeCl_3$	H_2O	$C_6H_5NH_3Cl$	$FeCl_3$	H_2O
1	26·47	3·69	69·84	95·59	0·42	4·08
2	24·17	5·22	70·61	75·86	3·75	20·39
3	22·43	5·37	72·20	65·95	7·18	26·87
4	23·62	5·34	71·04	89·45	3·41	7·14
5	21·13	6·78	72·09	61·15	14·03	24·82
6	17·58	8·95	73·47	62·53	15·04	22·43
7	14·53	12·12	73·35	58·64	15·75	25·61
8	13·07	12·52	75·00	51·79	15·37	32·84
9	10·87	15 93	73·10	63·35	17·09	29·56
10	10·49	17·70	71·81	36·14	17·95	45·91
11	9·19	19·96	70·85	38·05	19·08	42·87
12	8·46	22·13	69·41	64·61	18·42	26·97
13	7·79	23·78	68·43	52·22	20·51	27·27
14	7·87	25·80	66·33	54·49	26·26	19·25
15	7·19	26·58	66·23	24·69	24·88	50·43
16	6·87	24·22	65·91	20·66	25·96	53·38
17	6·90	27·68	65·42	48·77	37·52	13·71
18	6·26	29·75	63·99	47·81	36·60	15·59
19	6·25	30·38	63·37	56·07	36·49	7·44
20	5·61	32·51	61·88	50·68	30·50	11·82
21	5·01	36·76	58·23	48·95	38·12	17·93
22	3·98	37·58	58·44	44·48	34·62	16·90
23	3·85	38·75	57·40	46·68	36·95	14·37

From the data given in Tables 4 and 5, Fig. 2 was obtained.

From Figs. 1 and 2, it may easily be seen that under the conditions of our experiments there exist tow kinds of bouble salts, namely :

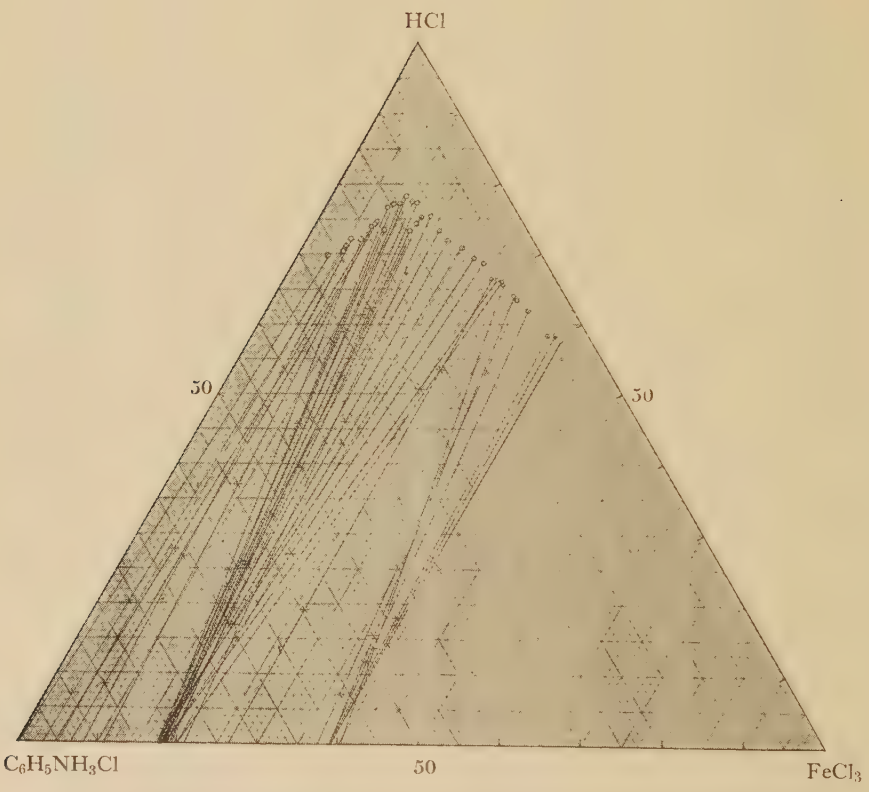
$$FeCl_3.6C_6H_5NH_3Cl \text{ and } FeCl_3.2C_6H_5NH_3Cl.$$

The former is in the form of yellowish crystals and the latter, bluish green needle-shaped crystals. These have also been, obtained by McKenzie, but the other two hydrated salts found by him could not be formed under the conditions of our experiments.

Summary.

The equilibrium of the system consisting of ferric chloride, aniline hydrochloride, hydrogen chloride and water at 25·0° was studied and the existence of the two double salts, $FeCl_3.6C_6H_5NH_3Cl$ and $FeCl_3 2C_6H_5NH_3Cl$, and the conditions under which they can exist have been ascertained.

Fig. 2.



On the Composition of Japanese Petroleum, I.

By

Shigeru Komatsu and Suehiko Kusumoto.

(Received June 12, 1923)

K. Kobayashi[1], S. Shimidzu[2], C. F. Mabery and S. Takano[3] and T. Katayama[4] have already investigated the composition of Japanese petroleum. The results of their investigations show that Japanese petroleum is composed for the greater part of hydrocarbons of the polymethylene series or naphthene. In addition to this, the geological survey of the oil fields in Japan[5], presented some evidence to support the above statement brought forward by the chemists. Although no doubts exist that polymethylene hydrocarbons constitute the main part of our petroleum, the studies made by these investigators provided no further knowledge of the exact constitution of the hydrocarbons, and moreover, were concerned specially with the fractions boiling at a higher temperature than 98°.

The authors, therefore, have undertaken the present study to isolate polymethylene hydrocarbons in pure condition and to ascertain their constitutions by chemical means.

The specimen used in this investigation was Nishiyama oil, Echigo, obtained by the kindness of Dr. T. Fujii. It was a dark green oil, having the sp. gr. 0.8230, and was composed of the following three portions :

Temp.	below 150°	150—300°	above 300°
Distillate %	23.2	47.3	29.5

1 Kogyo Kwagaku Zasshi, **5**, 321; **13**, 1277.
2 Ibid., **7**, 915.
3 Am. Chem. J., **25**, 297 (1901).
4 Kogyo Kwagaku Zasshi. **16**, 1341; **17**, 273.
5 C. Engler u. H. v. Höfer: Das Erdöl. II. 467 (1909); J. Takahashi: Scie. Reports Tohoku Imp. Univ. (III). **I**, 143 (1922).

The first portion was distillated under ordinary pressure three times in six successive portions :

TABLE I.

	Fraction.	Yield. %	$d_4^{25.1}$
1	32—50°	3.4	0.6525
2	50—70°	5.6	0.6841
3	70—90°	8.8	0.7196
4	90—120°	42.5	0.7529
5	120—150°	26.7	0.7773
6	above 150°	13.0	0.8151

2,350 grm. of the third fraction boiling at 70—90°, were shaken first with fuming sulphuric acid containing 7% SO_3, and afterwards with a mixture of sulphuric and nitric acids, being left in contact with the mixed acids for some hours, and then washed with water. It was then treated with 1% caustic potash solution, washed with water and dried over calcium chloride ; finally distilled on metallic sodium in a dephlegmator.

The oil freed from aromatic and unsaturated hydrocarbons by the treatments above mentioned, was fractionated three times at 10° intervals, and then twice at 5° intervals. The fractions boiling at 75—85° after five distillations, amounted to 757 grm. having sp.gr. 0.7340.

This portion was carefully distilled following S. Young's descriptions[1]. The oil to be distilled, was kept in a flask which connected with a six column dephlegmator, and was slowly distilled so that the drops of distillate fell at the rate of about one per second. After the 15th. distillation, the operation was continued at the rate of one drop of distillate every two seconds, and the liquid was collected in a flask cooled by ice water. The correction of boiling point for the barometric pressure during the operation was made, (0.04° per 1 m. m.) and the bulb of the thermometer was covered with a little cotton-wool to prevent super-heating.

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[1] Distillation principles and processes, 100 (1921).

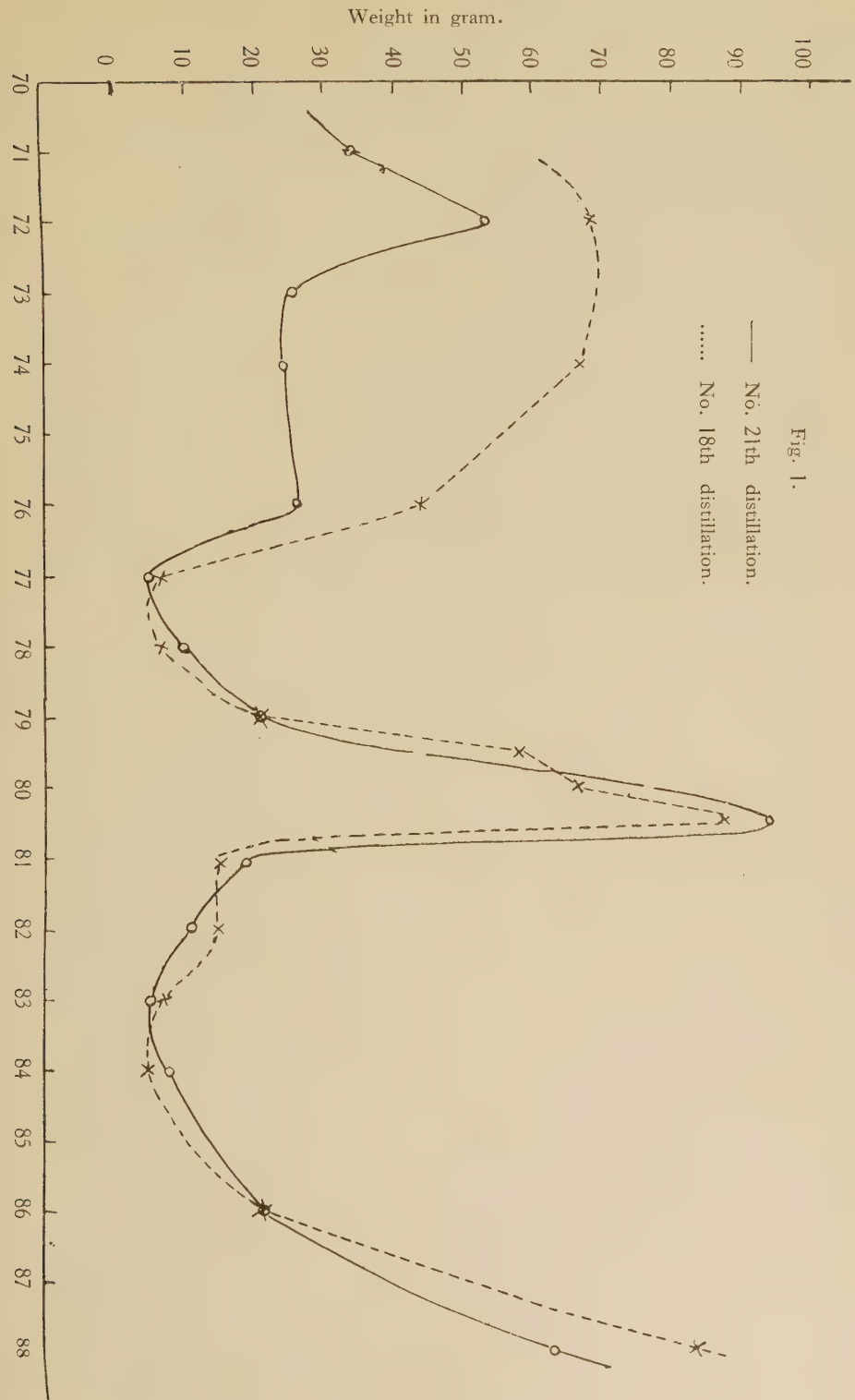
Weight in gram.
0
10
20
30
40
50
60
70
80
90
100
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
Temperature (C°)
—— No. 21th distillation.
..... No. 18th distillation.

Fig. 1.

The results of the 21st. fraction — the weight of each distillate, the ratio of weight to temperature range $\Delta w/\Delta t$, specific gravity, and index of refraction — are given in Table II.

In Fig. I. thc actual weight of distillate against the temperature of 18th. and 21st. distillations is plotted.

The temperature — weight curve of the 21st. distillation (Fig. I.) shows two maxima, one at 80—81°, and the other at 72°, and there appeared to be a maximum in the neighbourhood of 90°. As seen in Table I, the major portion of the oil boils at 70—90°, distills at 80—81°, and this fraction shows the largest index of refraction 1•414, and the highest density 0.765 ; and the fraction B. p. 71—72°, corresponding to the other maximum in the curve, indicates $=d_4^{25°}$ 0.7295, $n_D^{25°}=1.3965$.

TABLE II.

Fraction.	Temp.	Weight	%	$\Delta w/\Delta t$	$d_4^{25°}$	$n_D^{25°}$	M.R.
1	66—70°	66	9.4	14	—	—	
2	70—71°	34	4.8	34	0.7213	1.3930	
3	71—72°	54	7.7	54	0.7295	1.3965	
4	72—73°	25	3.5	25	0.7347	1.4000	
5	73—74°	25	3.5	25	0.7432	1.4035	
6	74—76°	27	3.8	13.5	0.7446	1.4045	
7	76—77°	5	0.7	5	0.7449	1.4050	
8	77—78°	10	1.4	10	0.7480	1.4072	
9	78—79°	21	3.0	21	0.7521	1.4090	27.54
10	79—79.5°	43	6.1	86	0.7567	1.4125	27.83
11	79.5—80°	76	10.8	152	0.7595	1.4130	27.36
12	80—80.5°	94	13.3	188	0.7652	1.4145	27.43
13	80.5—81°	19	2.7	38	0.7615	1.4130	27.36
14	81—82°	11	1.6	11	0.7568	1.4080	
15	82—83°	5	0.7	5	0.7526	1.4075	
16	83—84°	8	1.1	8	0.7437	1.4042	
17	84—86°	21	3.0	10.5	0.7413	1.4020	
18	86—88°	63	8.9	31.5	0.7201	1.3920	
19	over 88°	99	14.0	—	—	—	

Two portions correspond to methylcyclopentane and cyclohexane and they show a slight difference in density and index of refraction, compared with the same compounds obtained by other chemists, indicating the presence of some aliphatic hydrocarbons as an impurity. The purification of these fractions, however, was not continued as our apparatus was insufficient for the purpose.

CYCLOHEXANE.

The hydrocarbon B. p. 80—81°, isolated from Japanese petroleum, was also compared with respect to its physical constants with hexahydrobenzene prepared from pure benzene by the method of Prof. P. Sabatier, passing with pure hydrogen over reduced nickel heated at 180°, and purified by distillation[1].

TABLE III.

Observers.	B. p.	Density	Index of refraction.
Authors			
from petroleum	80—81°	$d_4^{25°} = 0.765$	$n_D^{25°} = 1.414$
,, benzene	80.3—81°	$d_4^{25°} = 0.7738$	$n_D^{25°} = 1.4195$
Markownikoff	80.5–81°(760 m.m.)	$d_4^{20°} = 0.7727$	—
Zelinsky	81—82°	$d_4^{20°} = 0.7764$	$n_D^{20°} = 1.4258$
Baeyer	79—79.5°		
Fortey, from			
american petroleum	80.55—80.65°	$d_4^{0°} = 0.7722$	
galician ,,	80.8°	$d_4^{0°} = 0.7903$	
Rosenthal	80.85°(760 m.m.)	$d_4^{20°} = 0.7764$	$n_D^{18°} = 1.43197$
R. Kissling	80.8°(760 m.m.)	$d_4^{20°} = 0.7788$	$n_D^{20°} = 1.4266$

It gave, on analysis, the results shown in Table IV. which agree fairly well those required for cyclohexane.

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1 C. R., **132**, 210, 566 (1901).
2 Ber. D. Chem. Ges., **28**, 577 (1895); **30**, 1225 (1897); Lieb. Ann., **302**, 1 (1898).
3 Ber. D. Chem. Ges., **28**, 1205 (1895); **30**, 390 (1897).
4 Ibid., **26**, 229 (1893); Lieb. Ann., **278**, 88 (1893).
5 J. Chem. Soc., **73**, 932 (1898).
6 Organische Verbindungen. 17, (1914).
7 Chemische Technologie des Erdöls, 31.

TABLE IV.

Fraction.	Temp.	Substance.	CO_2	H_2O	C%	H%
9	78—79°	0.1459grm.	0.4540grm.	0.1916grm.	84.86	14.62
,,	,,	0.1311	0.4082	0.1719	84.92	14.60
				mean	84.89	14.61
10	79—79.5°	0.1029	0.3211	0.1360	85.11	14.72
,,	,,	0.1148	0.3578	0.1484	85.37	14.40
,,	,,	0.1132	0.3537	0.1487	85.21	14.63
				mean	85.23	14.58
11	79.5—80°	0.1034	0.3234	0.1326	85.29	14.29
,,	,,	0.1031	0.3223	0.1341	85.27	14.49
,,	,,	0.1042	0.3257	0.1374	85.25	14.69
				mean	85.27	14.49
12	80—80.5°	0.1371	0.4297	0.1757	85.43	14.27
,,	,,	0.1149	0.3610	0.1493	85.69	14.49
,,	,,	0.1010	0.3166	0.1316	85.49	14.51
				mean	85.54	14.42
13	805.—81°	0.1280	0.4000	0.1635	85.23	14.22
,,	,,	0.1311	0.4105	0.1700	85.39	14.44
,,	,,	0.1032	0.3231	0.1354	85.39	14.62
				mean	85.34	14.43
14	81—82°	0.1392	0.4350	0.1816	85.23	14.53
,,	,,	0.1179	0.3689	0.1545	85.31	14.59
				mean	85.27	14.56
				Calc. for C_6H_{12}	85.62	14.38

According to Prof. P. Sabatier, reduced nickel heated at 300° serves as a catalyst for the dehydrogenation of cyclohexane which loses all the six hydrogen atoms of the ring and yields hydrogen and benzene. At a lower temparature, the reverse change occurs, the passage of hydorgen and benzene over reduced nickel heated at 180° resulting in the hydrogenation of benzene. The catalytic transformation of cyclohexane under the influence of reduced nickel into benzene, thus offers a convenient method for identification of the hydrocarbon as observed by N. Zelinsky[1] in russian petroleum using heated palladium black as a catalyst.

[1] Ber. D. Chem. Ges., **45**, 3678 (1912).

40 grm. of the substance B. p. 80—81°, were passed over reduced nickel at 300°, and the product possessing an aromatic odour and boiling at 77—81°, was fractionated into two portions. The yield was 24 grm.

	Fractions.	Yield	$d_4^{25°}$	$n_D^{25°}$
1.	77—79°	14 grm.	0.8178	1.4544
2.	79—81°	9 „	0.8288	1.4648

The second fraction showing the same specific gravity and index of refraction as pure benzene, was treated with a mixture of conc. nitric and sulphuric acids, yielding a compound which was purified by distillation. It boils at 210—211°, $d_4^{25°}=1.2074$, and gave, on analysis, the following results: C=58.59; 58.52; 58.61; H=3.99; 4.18; 4.42; N=11.26; 11.76; 11.95 (theory requirs C=58.51; H=4.10; N=11.39 for $C_6H_5NO_2$).

The physical constants and analytical results agree with those of nitrobenzene. It yields by reduction aniline which was confirmed by forming a double salt with platinum chloride and also other chemical reactions.

METHYLCYCLOPENTANE.

The substance isolated from the petroleum gave, on analysis, the elementary composition and showed the physical constants mentioned on the table V, with those of methylcyclopentane obtained by Markownikoff[1], Zelinsky[2], S. Young[3] and Aschan[4].

TABLE V.

Observers.	B. p.	Density.	Index of refraction.
Authors	71—72°	$d_4^{25°}=0.7295$	$n_D^{25°}=1.3965$
Markownikoff, synthesized	71.5—72°(742 m.m.)	$d_0^{0°}=0.76$	—
Baku oil	71—72°(755 m.m.)	$d_0^{0°}=0.7664$	—
Zelinsky	71.5—72.5°	$d_0^{20°}=0.7501$	—
Zelinsky and Moser	71°(743 m.m.)	$d_4^{19·5°}=0.7488$	—
Young	69.98—70.15°	$d_4^{0°}=0.7157$	—

1 Ber. D. Chem. Ges., **30** 1222 (1897).
2 Ibid., **30**, 389 (1897).
3 J. Chem. Soc., **73**, 913 (1898).
4 Ber. D. Chem. Ges., **41**, 2431 (1908).

For identification[1], 20 grm. of the oil B. p. 71—72°, in a flask were subjected to oxidation with 80 grm. fuming nitric acid (sp. gr. 1.51) and the solid reaction product deposited at the bottom of the flask, after 12 hours of reaction, was separated from the mother liquor by filtration. The yield was 3 grm. It melted at 97—120°. By repeated fractional crystallisation from its aqueous solution, it was separated into two compounds, one melting at 184—189° and the other at 98°—100°

The former compound, less soluble in water, was identified to be succinic acid by elementary analyis.

C=40.40 ; H=5.02, and also by molecular weight determination with $\frac{N}{10}$ NaOH solution, M. W.=117 (theory requires C=40.67 ; H=5•08 ; M. W.=118 for $C_4H_6O_4$).

The latter compound, more soluble in water, was also confirmed to be a mixture of oxalic and glutaric acids, varying carbon and hydrogen contents from 28.5 to 47.7 and from 3 to 5•3 respectively.

The volatile acid found in the mother liquor, was noticed to be acetic acid.

Methylcyclopentane was identified by oxidation with nitric acid, yielding acetic, oxalic and succinic acids with some glutaric acid as noticed N. Zelinsky and Gutt[2] and also by O. Aschan[3].

Thus, by repeated fractional distillation of petroleum, for about four months, we succeeded, as we had expected, in isolating these polymethylenes in fairly pure condition, and the examination of the other portion boiling about 90° will be reported in another article, with that of the fraction boiling below 70°.

April 1923. Laboratory of Organic and Biochemistry.

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[1] S. Nametkin : Ber. D. Chem. Ges. **42**, 1373 (1909). ; C. Engler, H. v. Höfer ; Das Erdöl. 1. 235 (1913) ; Markownikoff : Ber. D. Chem. Ges., **32**, 1445 (1899) ; **35**, 1584 (1902).

[2] Ber. D. Chem. Ges., **41**, 2431 (1908).

[3] Ibid., **31**, 1801 (1898).

Studies on Catalytih Action, IV.
A New Function of Reduced Copper.

By

Shigeru Komatsu

(Received July 12, 1923)

While engaged on the study of the camphor series, the author made use of the principle proposed by Prof. Paul Sabatier[1] for obtaining menthone by passing menthol on the reduced copper heated at 320°, which was prepared from copper oxide of the following composition, according to the direction of P. Sabatier[2].

$CuO = 99.89$; Fe_2O_3 = trace ; $Al_2O_3 = 0.025$;
$CaO = 0.046$; $MgO = 0.006$:

Contrary to expectation, the reaction product was found to consist of menthene instead of menthone; the product obtained from 30 grm. menthol, amounting to 25 grm. was separated from 1 c.c. of water formed simultaneously, and fractionated after drying with anhydrous sodium sulphate, in the following three portions :

1.	160—198°	9.3 grm.
2.	198—208°	3.9 ,,
3.	208—210°	11.7 ,,

The last fraction was found to consist of unchanged menthol, and the other fractions, after repeated fractional distillation, were separated into two portions :

1.	165—167°	4.7 grm.
2.	208—210°	4.5 ,,

The first fraction was confirmed by elementary analysis to consist of menthene, and the determination of the physical constants :

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1 La catalyse en chimie organique, 254 (1920).

2 Ibid., 18.

C=86.01; H=13.09 (theory requires C=86.87; H=13.13 for $C_{10}H_{16}$)
$d_4^{25}=0.8081$; $n_D^{25}=1.4456$.

So far as we could ascertain[1], when secondary alcohol passed through a heated glass tube, in presence of reduced copper, dehydrogenation was effected perfectly, yielding hydrogen and ketone, while metallic oxides such as thoria or alumina act as catalysts of dehydration, promoting the decomposition of the alcohol into olefine hydrocarbone and water. In the present case, however, it seems proper to ascribe the formation of menthene from menthol to the catalytic action of the reduced copper, in other word, metallic copper promotes the decomposition of menthol into menthene and water.

Does the reduced copper act, like thoria, as catalyst of dehydration at high temperature ? In order to ascertain the catalytic action of the reduced copper toward alcohols, 8 grm. copper oxide of the composition[2] were spread in a layer inside of a 75 cm. glass tube and reduced at 180° to a metallic copper on which ethyl alcohol purified by distillation on calcium oxide, was passed and the reaction tube was maintained at a temperature 320°. The vapours escaped from the reaction tube, condensed by passage through a condenser cooled with ice-water, the escaped gas from the condenser carried with it a small quantity of the liquid reaction product, which recovered by passing the gas through the second empty flask cooled with ice-water, and then through an absorption vessel containing bromine.

The reaction product in the condenser was found to consist of unchanged alcohol and acetaldehyde, and the latter was confirmed by Schiff's reagent and also identified by transforming it into aldelyde

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[1] Sabatier : La catalyse chimi. organ., p. 92, 250, 254 ; W. D. Bancroft ; Applied colloid chemistry, 44, 60 (1921) ; K. G. Falk : Catalytic action, 50, 156 (1922) ; C. Engler and J. Weissberg : Vorträge d. Autoxydation, 98, 149 (1904) ; P. Sabatier & B. Kubota : C. R., **172**, 733 : **173**, 17, 212 (1921) ; G. Woker : Die Katalyse, II, 397 (1915) ; G. G. Henderson : Catalysis in industrial chemistry, 121, 145 (1919) ; A. Skita : u. Kataly. Reduk. Org. Verb., 66,72 (1912) ; W. Ipatiew : Ber. D. Chem. Ges., **34**, 3587 (1901) ; **36**, 1993 (1903) ; **37**, 2961 (1904).

[2] CuO=99.88 ; Fe_2O_3=0.007 ; CaO=0.050 ; MgO=0.017.

ammonia. The other reaction product in the absorption vessel was recognised by its property of decolourising bromine to be ethylene, and this was confirmed by the analysis after purification by fractional distillation.

The substance B. p. 129—130°, gave on analysis Br = 85.23 (theory requires Br = 84.87 for $C_2H_4Br_2$).

It is a well-known fact that when ethyl alcohol[1] is passed through a heated glass tube, it begins to decompose at about 500°, two reactions taking place simultaneously, namely (1) dehydration of the alcohol, with the formation of water and ethylene, and (2) dehydrogenation, resulting in the product of hydrogen and acetaldehyde :

1. $C_2H_5OH = CH_2CH_2 + H_2O$.
2. $C_2H_5OH = CH_3CHO + H_2$

Such decomposition of the alcohol by heat may follow at a red heat but it shows no appreciable decomposition below 400°. In presence of catalysts these reactions can be brought about with greater velocity and at lower temperatures. Reduced copper, as the author has actually observed in the cases of menthol and ethyl alcohol acts to promote both reactions-dehydration and dehydrogenation, when alcohol is brought under the conditions described above, notwithstanding that it has the universal sanction of chemists reduced copper is the sole catalyst which perfectly induces dehydrogenation or hydrogenation.

On referring the literature[2], we have, however, noticed that diphenyl carbinol when heated to its boiling point (298°), suffers partial decomposition into water and benzhydrol ether, and the reaction seems to effected by a catalytic influence, transforming the carbinol by the action of heat (210—220°), in presence of copper powder, into the ether with the yield of 75% and accompanied with the formation of some diphenyl keton.

In the same manner, isopropyl alcohol B. p. 82°, from Kahlbaum,

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1 M. Berthelot and E. Jungfleisch : Traité élém. chimi. organ., **1**, 245 (1908) ; W. Ipatiew : Ber. D. Chem. Ges., **34**, 3579 (1901) ; **35**, 1047 (1902).

2 Ber. D. Chem. Ges., **36**, 2823 (1903) ; Beilstein : Handbuch d. Organ. Chem., 3rd. ed., II, 1077.

purified by distillation, was passed at the rate of one grm. per 20 seconds over the reduced copper heated at 300°.

Acetone formed by the reaction, was separated from unchanged alcohol by precipitating it as a mercury complex compound $(2HgSO_4 3HgO)_3 4CO(CH_3)_2$ with the Deniger reagent[1], which after separation and purification was analysed with the following results :

Hg = 77.5, theory requires Hg = 76.15.

The olefine hydrocarbone formed simultaneously with acetone was converted into the bromine derivative which after being fractionated into tow portions, was analysed :

1. 130—140° 0.3 grm.
1. 140—150° 0.5 grm.

1st. fraction : Br=80.58 ;

2nd. fraction : Br=80.03 ; theory requires Br=79.0 for $C_3H_6Br_2$.

It was confirmed that isopropyl alcohol, in the presence of the reduced copper, transforms by exposure to high temperature into acetone and propylene.

The mechanism of such decomposition of alcohols into aldehydes or ketones, in presence of the reduced copper, may be explained either by the dehydrogenation theory proposed by P. Sabatier[2] and also by H. Wieland[3], or by the dehydration theory.

In the oxidation, according to the latter view, a free oxygen atom inserts itself between the hydrogen atom and the carbon atom which the hydroxyl group is joined in the molecule of alcohol. α-Glycohol which is assumed to be formed in a moment as an intermediate product in the course of oxidation, being splitted off water, and its anhydride-aldehyde or ketone, resulted as will be seen in the following scheme :

$$RCH_2OH \longrightarrow R{\cdot}CH\begin{matrix}OH\\OH\end{matrix} \longrightarrow RCHO + H_2O$$

$$R_2CHOH \longrightarrow R_2C\begin{matrix}OH\\OH\end{matrix} \longrightarrow RCO + H_2O$$

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1 C. R., **127**, 963 (1898).

2 La catalyse en chimie organique, 58, 60 (1920).

3 Ber. D. Chem. Ges., **45**, 2606 (1912) ; 55, 3639 (1922).

The author, however, sides with the latter view for the explanation of the catalytic oxidation of the alcohol.

In generaly the direct transformation of alcohols into hydrocarbons and oxygen compounds by chemical means or pyrogenetic contact action may be represented in the following reactions :

$$2RCH_2CH_2OH = 2RCH{=}CH_2 + 2H_2O$$
$$2RCH_2CH_2OH = (RCH_2CH_2)_2O + H_2O$$
$$2RCH_2CH_2OH = 2RCH_2CHO + 2H_2O$$

6 mol. 5 mol. 5 mol.

When the reactions proceed simultaneously as shown in the equations, the quantity of water generated by the reactions should be of the same molecular proportion as that of the substances formed by the transformation.

In order to see, if there may exist some relation between the amount of water and that of the compounds which were formed by the reaction, the author carried the experiment of passing 18 grm. hexahydrophenol over the reduced copper heated at 320°, during an interval of 8 hours. One grm. of water, 15.5 grm. oily substance $d_4^{25°} = 0.8874$, were obtained as a reaction product, and the latter separated from water, dried with anhydrous sodium sulphate, was subjected to fractional distillation under ordinary pressure :

Fraction	Yield	
	in grm.	in mol.
1. 80—90°	2.4	0.024
2. 90—150°	0.1	
3. 150—165°	4.8	0.024
4. 175—200°	0.6	
5. above 200°	0.2	0.001
		0.048

The first fraction again purified by repeated distillations with metallic sodium and the fraction B. p. 82—83°, with the yield 2 grm. was confirmed to consist of tetrahydrobenzene by its analysis and also by measurement of the physical constants :

C=87.84 ; H=12.29 ; d_4^{25}=0.8076 ; n_D^{25}=1.440.

The third fraction assumed to be a mixture of hexahydrophenol and cyclohexanone, was treated with hydroxylamine to separate the latter substance as an oxime, from the former. The oxime thus isolated amounting to 1.2 grm. (69% of the fraction) was purified by recrystallization from petroleum ether solution, and was analysed with these results :

C=64.26 ; H=9.95 ; N=11.5 (by Kejeldal's method), theory requires C=63.66 ; H=9.80 ; N=12.38 for $C_6H_{11}NO$.

The elementary analysis and M. p. 98—89°.5, agree with those of cyclohexanone oxime[1].

The analytical results of the 4th and 5th fractions are as follows :

4th. fraction : C=74.4 ; H=9.4 ; O=16.2 (by difference).

5th. ,, C=77.4 ; H=9.9 ; O=12.7 (,, ,,).

It seems that the 5th fraction by the analytical results, consists mainly of di-hexahydrophenyl ether[2] requiring C=79.1 ; H=12.1 ; O=8.8.

The yield of the compounds being 0.048 mol., agrees approximately with that of water (0.055 mol) generated simultaneously during the reaction. Hence, we have to confess that the formation of unsaturated hydrocarbons by dehydration of alcohol, was actually effected by the catalytic action of reduced copper as it promotes the oxidation of alcohol. Though the mechanism of the reactions under such conditions, was not at all decided, the author suggests that the reduced copper surely promotes the dehydration of alcohol.

It may naturally be considered that the reduced copper is also capable, under different conditions, of exercising a catalytic influence in promoting the oppsite reaction of dehydration. The reactions of the hydration of nitriles usually brought about with the aid of catalysts such

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1 A. Baeyer : Lieb. Ann., **278**, 102 (1893).

2 W. Ipatiew and O. Philipow : Ber. D. Chem. Ges., **41** 1001 (1908) ; S. Komatsu and S. Kumamoto : These Memoirs, **6**, 48 (1922).

as thoria and acids, which were also accelerated in presence of reduced copper, resulted in amides from the mixturs of nitriles and water, these results will be communicated in the next article.

The formation of α-campholenic acid[1] from camphoroxime, reduced copper and hydrogen at 200°, of benzoic acid[2] from acetophenonoxime and of menthonyl acid[3] from menthonoxime under the same conditions, should be explained by the same mechanism which was applied in the reaction forming benzamide from benzonitrile and water at 200° in presence of the reduced copper, namely, the hydration of nitriles which were formed as an intermediate compound from the oximes by the Beckmann rearrangement or the so-called nitrile decomposition[4], nitriles by addition of water transformed into acid amides and then into acids successively.

The new catalytic action of the finely divided reduced copper will be studied further in my laboratory.

The author is indebted to Messrs. M. Ishimasa and M. Kurata for assistance in some of the experiments.

May 1923, Laboratory of Bio-and Organic Chemistry.

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1 S. Komatsu and S. Yamaguchi : These Mencoiss **6**. 245 (1923).
2 Unpublished work by Yamaguchi.
3 Unpublished work with S. Kurata.
4 A-Kötz and O. Wunstorf : J. prak. Chem., (2), **88**, 519 (1913).

Condensation of Nitriles with Thiamides II. Acetonitrile with Thiobenzamide; and Benzonitrile with Thioacetamide

By

Seiichi Ishikawa.

(Received July 11,1923)

In the previous communication[1] it was reported that benzonitrile and thiobenzamide combine together to form benziminoisothiobenzamide, when their ethereal solution is saturated with dry hydrogen chloride. Now in extending the study to the condensation of acetonitrile with thiobenzamide a quite unexpected result was found. The condensationproduct then obtained was not acetiminoisothiobenzamide as was expected but benziminoisothiobenzamide, the very substance which was reported previously as the condensation-product of benzonitrile with thiobenzamide. At first I suspected that this unexpected result was brought about by benzonitrile, with which the ethereal solution had become admixed by some mistake. So that the experiment was repeated once more all the materials used being strictly examined and carefully purified. But the experiment always resulted in the production of the same substance, leaving no room to doubt that what is produced by passing dry hydrogen chloride into an ethereal solution of acetonitrile and thiobenzamide is nothing but benziminoisothiobenzamide. The only substance conceivable as the source of benzonitrile which entered into the condensation, is thiobenzamide from which it might be considered to have been produced either by simple decomposition or by an interaction with acetonitrile. To decide which

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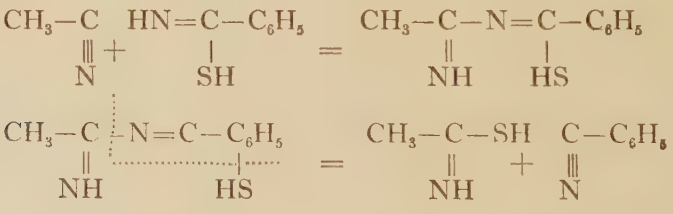
1 These Memoirs, V, 179 (1921).

was really the case, dry hydrogen chloride was saturated in a cooled ethereal solution of thiobenzamide as is described in experiment II. The yellow colour of the solution remained unchanged ; no hydrogen sulphide was evolved ; no sign of the decomposition of the thiamide into benzonitrile and hydrogen sulphide could be observed. When, however, acetonitrile was added to it the colour of the solution began to change gradually from yellow to reddish yellow, showing that condenstaon between benzonitrile and thiobenzamide had now set in.

As to the mechanism of the reaction by which benzonitrile is produced from acetonitrile and thiobenzamide the author ventures to explain it on the assumption, that acetonitrile and thiobenzamide first condense with each other in the same manner as in the condensation of benzonitrile and thiobenzamide, and this condensation-product because of its instability decomposes into benzonitrile and thio-acetamide as is seen in the following equation :



If this explanation is correct thio-acetamide must be found in the solution, in which the condensation took place. So the solution was examined by treating it in the manner described in experiment III, and thio-acetamide was really isolated.

While in the condensation of benzonitrile with thiobenzamide the yield of benziminoisothiobenzamide is nearly quantitative, the quantity of the same condensation-product formed by the interaction of acetonitrile and thiobenzamide is so small, that only about 14% of the thiobenzamide originally used can be regaded as having taken part in the condensation. The doubt as to what causes such a discrepancy between the two condensations was made clear on studying the condensation of benzonitrile with thio-acetamide. When the ethereal solution of benzonitile and

thioacetamide was saturated with dry hydrogen chloride as usual, benziminoisothiobenzamide was also formed as the condensation-product, and at the same time a lot of thiobenzamide was produced. From the quantities of the condensation-product and thiobenzamide it was roughly calculated that about 71% of the benzonitrile used had changed into thiobenzamide (Experiment IV). On considering the above two relations together it may be concluded that the reaction between acetonitrile and thiobenzamide is a reversible one which attains an equilibrium when about 20% of them changes into benzonitrile and thioacetamide thus :

$$\underset{\text{N}}{\overset{\|}{\text{CH}_3\text{—C}}} + \underset{\text{HS}}{\overset{|}{\text{NH=C—C}_6\text{H}_5}} \rightleftarrows \underset{\text{NH}}{\overset{\|}{\text{CH}_3\text{—C—SH}}} + \underset{\text{N}}{\overset{\|}{\text{C—C}_6\text{H}_5}}$$

80% 20%

All efforts to isolate the intermediate condensation-products

$$\underset{\text{NH}\quad\text{HS}}{\overset{\|\quad|}{\text{CH}_3\text{—C—N=C—C}_6\text{H}_5}} \qquad \text{and} \qquad \underset{\text{NH}\quad\text{HS}}{\overset{\|\quad|}{\text{C}_6\text{H}_5\text{—C—N=C—CH}_3}}$$

were found fruitless.

EXPERIMENTAL PART

EXPERIMENT I.

2·0 grams of acetonitrile and 6·64 grams of thiobenzamide (molecular proportion) were dissolved in 200 c.c. of ether, and into this solution dry hydrogen chloride was conducted when the solution gradually acquired a reddish tint which became the deeper the more hydrogen chloride was passed. As the ethereal solution thus saturated with hydrogen chloride produced no crystalline substance even after 12 hours an equal volume of ether was added, whereupon orange-coloured crystals separated out. The crystals were gathered, washed with ether and treated with a soda solution ; the substance thus liberated was extracted with benzene and crystallized from it by addition of petroleum ether. About 0·2 gram of red prismatic crystals melting at 75° was thus

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1 These Memoirs, V, 179(1921).

obtained. Their physical and chemical properties were all found to be quite identical with those of benziminoisothiobenzamide[1] formerly reported as formed by the condensation of benzonitrile with thiobenzamide. The result of the experiment was quite unexpected, but it was confirmed by repeating the experiment with the utmost care. The condensation-product was analysed with the following results :

1. 0•3464 grm. hydrochloride gave 0•1803 grm. AgCl
2. 0•2354 grm. ,, ,, 0•1188 grm. ,,

	Found		Calc. ($C_{14}H_{12}N_2S.HCl$)
	(1)	(2)	
Cl	12•88	12•49	12•84 %

3. 0•2400 grm. the substance required 20•9 c.c. $\frac{1}{10}$N-I for oxidation and gave 0•2336 grm. dibenzenylazosulphime.

	Found	Clac. ($C_{14}H_{12}N_2S$)
$\frac{1}{10}$N-I	20•9	20•0 c.c.
$C_{14}H_{10}N_2S$	0•2336	0•2380 grm.

The molecular weight of the condensation-product was determined by the cryoscopic method, using its benzene solution.

Benzene 17•6826 grm., the substance 0•3435 grm., freezing point depression 0•417°

	Found	Calc. ($C_{14}H_{12}N_2S$)
Mol. Weight	247	240

EXPERIMENT II.

To see whether benzonitrile could be produced from thiobenzamide by the action of hydrogen chloride, 0•83 grm of thiobenzamide was dissolved in 50 c.c. of ether, and into this ethereal solution dry hydrogen chloride was passed. The solution became turbid after about an hour but again clear on further saturation with hydrogen chloride, and no colour-change was observed. This cleardy points out that no benzonitrile was liberated in the solution. For, if some benzonitrile were liberated, it would condense with thiobenzamide so as to yield benziminoisothiobenzamide, which must impart a reddish colour to the solution.

When the solution after standing over-night was mixed with the calculated quantity of acetonitrile, the colour of the solution began to change into reddish yellow, showing that the condensation-reaction between benzonitrile and thiobenzamide had now set in. It is, therefore, evident that benzonitrile is the product of the reaction between thiobenzamide and acetonitrile, but not that of the decomposition of thiobenzamide itself.

EXPERIMENT III.

If the reaction between acetonitrile and thiobenzamide actually proceeds in such a manner as the author assumes it to be, thio-acetamide must be detected as one of the reaction-products. To confirm this, the following experiment was conducted. 10•0 grams of thiobenzamide and 2•99 grams af acetonitrile (molecular proportion) were together dissolved in ether and the solution was treated with dry hydrogen chloride as described before. By this treatment about 0•42 gram of benziminoisothiobenzamide was produced leaving 8•38 grams of thiobenzamide unchanged. To isolate thioacetamide from the ethereal solution in which the above condensation-reaction took place ether and hydrogen chloride were driven out by passing carefully dried air into the solution. Ether was then added to the residue and again driven out, and this process was repeated several times. The residue, still acidic, was digested with water, and the aqueous solution obtained was extracted with ether. Ether was then driven out from the ether extract, and the residue was again digested with water. On evaporating the aqueous extract a colourless crystalline substance mixed with thiobenzamide was obtained. It was washed with a small quantity of ether and recrystallized from ether. It was found to crystallize in plates, to melt at 107—108° and to precipitate silver sulphide from a silver nitrate solution. These properties and others all agree well with those of thio-acetamide.

In this experiment 0•42 gram of benziminoisothiobenzamide and 8•38 grams of thiobenzamide were obtained from 10•0 grams of thioben-

zamide. It is, therefore, calculated that 14% of the thiobenzamide originally used changed into benzonitrile. This percentage could not be much increased by using twice as much thiobenzamide.

EXPERIMENT IV.

7·5 grams of thio-acetamide and 10·31 grams benzonitrile (molecular proportion) were dissolved in 100 c.c. of ether, and into this solution, cooled with ice, dry hydrochloric acid gas was passed. Some white crystalline substance was observed to crystallize out, but it gradually disappeared as the solution became saturated with hydrogen chloride, and at the same time the solution was coloured reddish yellow. On keeping the solution in a cooled chamber for 24 hours, its colour changed entirely to red. The ether was now driven out from the solution by passing dry air into it, and the residue (I) was repeatedly washed with ether and then treated with a soda solution. The free condensation-product liberated was extracted with ether and recrystallized from a mixture of benzene and petroleum ether. The ethereal solution obtained by washing the residue (I) with ether was evaporated, and the residue was treated with a small quantity of cold water to remove thio-acetamide and finally was dissolved in hot water from which thio-benzamide was obtained as needle crystals on cooling. By this process about 0·62 gram of the condensation-product and 9·104 grams of thio-benzamide were obtained. They were each analysed with the following results :

0·1851 grm. hydrochloride of the condensation-product gave 0·0954 grm. AgCl

	Found	Calc. ($C_{14}H_{12}N_2S.HCl$)
Cl	12·75	12·84%

0·5013 grm. thiobenzamide (m. p. 114—115°) gave 0·8210 grm. $BaSO_4$ when oxidized with $KMnO_4$.

	Found	Calc. (C_7H_7NS)
S	22·47	23·31 %

The value of sulphur was found a little lower than the theoretical, as a part of the thiobenzamide was transformed into dibenzenylazo-sulphime which resisted further oxidation.

The author wishes to express his sincere thanks to Prof M. Matsui at whose suggestion the work was carried out.

Studies on Camphor Oils Part 1
On the Reaction between Camphor Red Oil[1] and Sulphuric acid.

By

Kashichi Ono.

(Received April 11, 1923)

According to Japanese Patent 37,119(1920)[2] N. Sugiyama obtained terpinhydrate from camphor red oil by treating it with sulphuric acid. As comphor red oil contains a large amount of terpineol which easily changes into terpinhydrate[3] by the action of a dilute sulphuric acid it is quite natural that the oil forms terpinhydrate when treated with sulphuric acid. But camphor red oil contains safrol, camphor and sesquiterpene beside terpineol, and these substances are expected to have some influence upon the hydration reaction of terpineol. The present work was undertaken to know what influence they have and how it is overcame in order to secure the best yield of terpinhydrate.

1. *Action of Sulphuric acid upon Terpineol mixed with safrol, camphor and sesquiterpene.*

[with Kozo Adachi]

Materials having following physical properties were used in the experiment :

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1 E. Gieldemeister u. Fr. Hoffmann, Die ätherischen Öle, Bd II, 485 (1913).

2 Chem. Abstr., 15, 3851 (1921).

3 F. Tiemann u. R. Schmidt., Ber. D. chem. Ges., **28**, 1781 (1895) ; O. Aschan, Joun. chem. Soc., **116**, 1. 336 (1919).

(1) Liquid-terpineol

Specific gravity 0•9356 (20°), refractive index 1•4822 (21°), acetyl value 276•82.

(2) Safrol

Specific gravity 1.1064 (15°), refractive index 1•5386 (21°),

(3) d-Camphor

Melting point 186°, $[\alpha]_D$ 39•37

(4) Sesquiterpene[1]

Specific gravity 0•9267 (16°), refractive index 1•5110 (14•5°)

General Procedure. 100 c.c. of material were mixed with 100 c.c. of sulphuric acid(45 %), and the mixture was vigorously shaken for 24 hours at 12—15°. After separating the crystalline substance from the reaction product by filtration, the filtrate was neutralized with sodium carbonate, and the crystalline substance first separated and the solid matter isolated by neutralization were mixed together and washed several times with petroleum ether. The crystallime mass thus purified, after having been dried in air, was weighed.

TABLE I.

Liquid-terpineol c.c.	Safrol c.c.	Camphor gr.	Sesquiterpene c.c.	Terpinhydrate. gr.
100	—	—	—	94.0
50	50	—	—	47.2
50	—	50	—	46.1
50	—	—	50	50.1
30	—	30	40	22.5
30	30	30	10	19.0
30	30	—	40	23.6
30	—	—	70	22.7
20	—	—	80	14.6
10	—	—	90	5.6
10	80	10	—	5.3
10	40	20	30	6.1

[1] F. Semmler u. J. Rosenberg, Ber. D. Chem. Ges., **46**, 768 (1913).

2. *Action of sulphuric acid upon Camphor Red Oil.*

〔with Kozo Adachi〕

As the formation of terpinhydrate from impure terpineol depends upon the concentration of the terpineol, it is essential for preparation of terpinhydrate to use camphor red oil containig as much terpineol as possible. Natural camphor red oil (Sp. gr. above 1.2000) containing safrol (40%), terpineol (17—19%) and camphor (3—4%) was therefore cooled with a freezing mixture to remove safrol as a crystalline mass, and the liquid portion thus freed from safrol and having the following physical properties was used in the experiment.

Specific gravity 0.9046(15°), refractive index 1.4942(22°), optical rotation + 8.10°, acid value 0.483, ester value 5.882, saponification value 6.365, acetyl value 122.64.

(a) Influence of the Concentration of Sulphuric acid.

Camphor red oil treated as above	100 c.c.
Sulphuric acid	100 c.c.
Time of reaction	10 hours
Temperature	12—15°

TABLE II.

Concentration of sulphuric acid	Terpinhydrate	Yield of terpinhydrate	Acetyl value of oily part
%	gr.	%	
30	1.2	2.94	120.92
35	6.4	15.61	108.09
40	12.3	30.06	87.26
45	18.3	44.64	63.85
50	15.3	37.39	45.29
60	0	—	3.25

The yield of terpinhydrate was calculated as follows :

$$\text{Yield of terpinhydrate} = \frac{\text{terpinhydrate}}{33.22} \times 100$$

33.22 is the quantity of terpineol in grams, calculated from the acetyl value of the camphor red oil used in the experiment.

(b) Influence of Time Reaction.

Camphor red oil	100 c.c.
Sulphuric acid	100 c.c.
Temperature	12—15°

TABLE III.

Concentration of sulphuric acid %	Time hr.	Terpinhydrate gr.	Yield of terpinhydrate %	Terpin-hydrate/Time gr./hr.	Acetyl value of oily part
35	10	6.4	15.61	0.64	108.09
35	30	14.3	34.95	0.476	85.51
40	6	10.6	25.91	1.76	94.82
40	10	12.3	30.06	1.23	87.26
40	20	19.5	47.66	0.975	60.21
40	30	20.6	50.35	0.686	57.26
45	3	10.4	25.42	3.46	88.42
45	6	17.2	42.04	2.86	66.46
45	10	18.3	44.63	1.83	63.85
45	20	16.0	39.11	0.80	48.06
50	10	15.3	37.39	1.53	45.29
50	20	8.0	15.99	0.40	26.8

(c) Influenec of Temperature.

Camphor red oil	100 c.c.
Sulphuric acid	100 c.c.
Time of reaction	10 hours

TABLE IV.

Concentration of sulphuric acid %	Temperature	Terpinhydrate gr.	Yield of terpinhydrate %	Acetyl value of oily part
40	12—15°	12.3	30.06	87.26
40	0°—(—3°)	12.2	29.82	90.04
45	12—15°	18.3	44.63	63.85
45	0°—(—2°)	20.7	50.59	87.13
45	60—70°	0	—	12.86

3. *Esters in the Canphor Red Oil.*

200 c.c. of the camphor red oil were mixed with the same volume of sulphuric acid (45 %), and after the mixture had been vigorously shaken for 10 hours at 12—15° the product was treated in the same

manner as in the general procedure. The crude yield of terpinhydrate was 32.6 grams. When purified by recrystallizning twice from alcohol, it was obtained in the form of colorless prisms, melting at 116—117°.

It was analysed with the following results :

0.1496 gr. substance gave 0.3464 gr. CO_2 and 0.1579 gr. H_2O.

	Found	Cal.($C_{10}H_{22}O_3$)
	%	%
Carbon	63.07	63.09
Hydrogen	11.78	11.66

The oily liquid portion (about 154.6 c.c.) obtained after neutralization of sulphuric acid by sodium carbonate and separated from terpinhydrate showed the following physical characters :

Specific gravity 0.9783 (23°), optical rotation + 17.78', refractive index 1.4931 (21°), acid value 0.213, ester value 5.881, saponification value 6.094, acetyl value 65.03.

The ester value of the oil was found to remain unchanged even after its reaction with sulphuric acid. If the ester consists of a lower fatty acid such as formic— or acetic acid, it must be hydrolized by sulphuric acid and produce terpinhydrate as is seen from the result of the following experiment.

50 c.c. of terpinylacetate [Specific gravity 0.9697 (14°), refractive index 1.4685 (21°), and ester value 265.75] were treated with the same volume of sulphuric acid (45 %) in the manner analogous to that described in the previous experiment, and the terpinhydrate thus obtained was recrystallized from alcohol. It melted at 116—117° and its properties were all found to be identical with those of terpinhydrate.

To isolate the fatty acid which forms ester in the camphor red oil the following experiment was conducted.

2000 c.c. of the camphor red oil were shaken several times with a sodium carbonate solution till its acidic reaction altogether disappeared. It was then washed with water and was mixed with 700 c.c. of an alcoholic potash solution (10 %), and the mixture was heated for 6 hours on the water bath. After distilling off the greater part of the alcohol, the residual oily part was repeatedly extracted with water, and the water

extract was evaporated to a small volume. It was then acidified with sulphuric acid and the oily substance separated was extracted with ether. On distilling off the ether, a dark brown viscous oily substance was obtained which was dissolved in 3% sodium hydroxide solution, and the part soluble in sodium hydroxide was again acidified with sulphuric acid. The oily substance separated was once more extracted with ether, and dried. The reddish yellow ethereal extract was treated with charcoal for decolourization and evaporated, and the residue was finally subjected to fractional distillation under 10—12 m.m. pressure.

Fraction	Temperature	Distillate	Refractive index
a	up to 140°	3.2	1.4328 (21°)
b	140—150°	1.0	1.4339 (25°)
c	150—160°	2.3	1.4234 (62°)
d	160—167°	4.9	1.4270 (65°)
e	above 167°	2.6	—

The fraction (a) was redistilled under 10—12 m.m. pressure. and a fraction distilling at 122—126° was obtained in a form resembling yollowish butter (refractive index 1.4307 (21°) when cooled with a freezing mixture. It was analysed as its silver salt.

0.1649 gr. substance gave 0.2346 gr. CO_2, 0.0953 gr. H_20, and 0.0719 gr. substance gave 0.0313 gr. Ag.

	Found	Cal.($C_8H_{15}0_2Ag$)
	%	%
Carbon	38.80	38.04
Hydrogen	6.46	6.02
Silver	43.53	42.98

The fraction (d) was redistilled under 14—15 m.m. pressure, and fraction boiling at 174—176° was collected. Crystals obtained by pressing the distillate on a tile were recrystallized from alcohol when silky crystals, melting at 43—44° [refractive index 1. 4259 (64°)] were produced.

This silky substance was analysed with the following results : 0.1641 gr. substance gave 0.4306 gr. CO_2 and 0.1780 gr. H_2O.

	Found	Cal. ($C_{12}H_{24}O_2$)
	%	%
Carbon	71.55	71.93
Hydrogen	12.12	12.09

From the above results the two acids are considered to be caprylic—and lauric acid, respectively. Both acids[1] were known to exist in camphor oil, especially lauric acid in the " Kusu—oil " (camphor seed oil) as glycerides.

Camphor red oil, which has no ester value was next examined,

Specific graviry 0.9801 (20°), refractive index 1.4980 (22°),

acid value 0, ester value 0, acetyl value 121.83.

200 c.c. of the oil having the above properties were treated with the same volume of 45 % sulphuric acid in a manner analogous to that described in the previous experiment, and 38.9 grams of crude terpinhydrate was produced. The oily liquid portion (161.3 grams) showed the following physical characters :

Specific gravity 0.9779 (21°), refractive index 1,4920 (21°),

acetyl value 67.81.

Summary

1. Terpinhydrate was observed to be produced from camphor red oil by the catalytic hydration of sulphuric acid.

2. It was confirmed experimentally that the yield of terpinhydrate depends upon the concentration of the terpineol existing in the oil.

3. 45% sulphuric acid gave the best yield of terpinhydrate.

4. For the preparation of terpinhydrate from camphor red oil the most suitable time of reaction was determined to be 10 hours when 45% sulphuric acid is used.

5. The temperature should be kept below 20°.

6. It was found that ester value of the camphor red oil does not change by the action of sulphuric acid.

7. Caprylic—and lauric acid were isolated by saponifying terpinyl-ester existing in the camphor red oil.

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[1] Bericht von Schimmel & Co., Oct. 21, (1902) ; K. Kafuku, Journ. chem. Ind. (Tokyo), 19, 815 (1916).

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